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A STUDY OF THE REACTIONS OF VARIOUS INORGANIC AND ORGANIC SALTS IN PREVENTING SCALE IN STEAM BOILERS

A REPORT OF AN INVESTIGATION

CONDUCTED BY

THE ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS

IN COÖPERATION WITH

THE NATIONAL ALUMINATE CORPORATION

BY

FREDERICK G. STRAUB

BULLETIN No. 283
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FREDERICK G. STRAUB
SPECIAL RESEARCH ASSISTANT PROFESSOR OF
CHEMICAL ENGINEERING

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A STUDY OF THE REACTIONS OF VARIOUS INORGANIC AND ORGANIC SALTS IN PREVENTING SCALE IN STEAM BOILERS

I. Introduction

1. *Purpose of Investigation.*—Engineers in power plants are continuously facing the problem of scale prevention in steam boilers. In attempting to prevent the formation of scale it is essential that they have available data from which to formulate or select the particular treatment required. The purpose of this investigation has been to study methods of chemical treatment which might be used for the prevention of the various types of scale which form in steam boilers.

Since the chemical treatment of boiler water may be readily classified under two distinct headings, inorganic and organic, it was thought advisable to divide this study into two parts. Therefore, the results of this work will be discussed under the two main headings, Inorganic and Organic.

2. *Sponsor of Investigation.*—The material embodied in this bulletin results from a research sponsored at the University during the period between April 1933 and April 1935 by the National Aluminate Corporation.

3. *Acknowledgments.*—The investigation was conducted as part of the work of the Engineering Experiment Station of the University of Illinois, of which Dean M. L. Enger is the Director, and is one of the researches in Chemical Engineering conducted under the direction of Dr. D. B. Keyes, Professor of Chemical Engineering.

Part of the work dealing with the removal of silica from solution and the solubility of silicates was done by Mr. J. W. Nelson as a thesis requirement for his B.S. and M.S. degrees in Chemical Engineering.

Part of the work dealing with the formation of solid silicates was done by Mr. A. O. Blatter as a thesis requirement for his M.S. degree in Chemical Engineering.

Part of the work covering the laboratory tests of organic treatment was done by Mr. R. V. Green as a thesis requirement for his B.S. degree in Chemical Engineering.

The work covering the composition of the organic materials and the preparation of the organic materials tested was done by Mr. J. M. Cross.

The author wishes to express his appreciation of the excellent manner in which these men, and others who have been employed in doing the more routine work, have assisted him throughout this investigation.

II. Inorganic Studies

4. *Method of Investigation of Effect of Inorganic Salts.*—The purpose of this investigation has been to study methods of inorganic water treatment which might be used for the prevention of the various types of scale which form in steam boilers. The compositions of the different waters which are utilized for steam generation vary to such an extent that many different types of scale are encountered. In order to study the prevention of these scales, it was thought advisable to divide this portion of the investigation into a study of the different scales; a study has therefore been made of the application of inorganic treatment to the prevention of silicate and sulphate scale.

Since scale results from a combination of the several ions involved to produce a solid which forms on, or adheres to, the heating surfaces of the boiler, it appears logical to study the prevention of scale by determining the solubility of the scale-forming materials in solutions, and under conditions similar to those encountered in actual practice. With these data available, it is possible to predict which solid will form in the boiler, and to treat the boiler water so as to cause a non-scale-forming solid to form in preference to a scale-forming one. With this information available, tests could be run in small test boilers to determine the workability of any theories developed. Since test bombs for the determination of solubility, as well as a small scale testing boiler, were available,* it was decided to use these for the tests involved.

This portion of the investigation has been divided into two parts: first, a study of the prevention of silicate scale; and second, a study of the prevention of sulphate scale. The results obtained will be reported under these two headings.

5. *Prevention of Silicate Scale.*—Since the silica scale which forms on the heating surfaces of a steam boiler comes from silica present in the boiler water, it appears that a logical method of preventing the scale would be either removing the silica from solution or keeping it in a form which is soluble and which will not precipitate in the

*See Bulletin 261, Engineering Experiment Station, University of Illinois.

boiler. In the present investigation this phase of the problem has been studied under the following divisions:

(A) Removal of silica from Solution at Boiler Temperatures
(B) Formation of Solid Silicates
(C) Solubility Studies of Silicates

(A) Removal of Silica From Solution at Boiler Temperatures

The tests which have been conducted in order to study the removal of silica from solution at boiler temperatures have been run in the steel bombs described in Bulletin No. 261.* The desired solutions and solids were added to the large bomb and held under pressure at the desired temperature until equilibrium had been reached, and then sampled by passing the solution through a filter into the smaller bomb. After the sampling, the bombs were removed from the constant temperature furnaces, and, when cooled, the solution was drawn from the smaller bomb and analyzed.

The solutions containing the soluble silicate were made by adding definite amounts of a standard sodium silicate solution, along with the other desired chemicals, to the solution in the lower bomb. The standard sodium silicate solution was prepared by diluting sodium silicate (specific gravity 1.41) with boiled distilled water. The composition of the solutions at the beginning of the tests was determined by analysis. The alkalinity was determined by titration, the sulphate by precipitation as barium sulphate, the silica by either the colorimetric method or by precipitation and weighing as SiO_2, and the aluminate by precipitation and weighing as Al_2O_3.

The tests conducted, and the numbers of the tables giving the results of these tests, are as follows:

Table No.	Solid Added	Solution Added
1	None	Sodium silicate, hydroxide
2	None	Sodium silicate, aluminate, hydroxide
3	Calcium sulphate	Sodium silicate, hydroxide
4	Calcium carbonate	Sodium silicate, hydroxide
5	Calcium carbonate	Sodium silicate, aluminate, hydroxide
6	Calcium carbonate	Sodium silicate, fluoride, hydroxide
7	Calcium carbonate	Sodium silicate, cryolite, hydroxide
8	Calcium fluoride	Sodium silicate, hydroxide
9	Tri-calcium phosphate	Sodium silicate, hydroxide

*"The Cause and Prevention of Calcium Sulphate Scale in Steam Boilers," Univ. of Ill. Eng. Exp. Sta. Bul. 261, 1933. See also Jour. Am. Chem. Soc. 24-914, 1932.

Table No.	Solid Added	Solution Added
10	Tri-calcium phosphate	Sodium silicate, aluminate, hydroxide
11	Tri-calcium phosphate	Sodium silicate, fluoride, hydroxide
12	Tri-calcium phosphate	Sodium silicate, cryolite, hydroxide
13	Magnesium oxide	Sodium silicate, hydroxide
14	Magnesium oxide	Sodium silicate, hydroxide, sulphate
15	Magnesium oxide	Sodium silicate, hydroxide, sulphate, chloride
16	Magnesium oxide	Sodium silicate, aluminate, hydroxide
17	Magnesium oxide	Sodium silicate, aluminate, hydroxide, sulphate
18	Magnesium oxide	Sodium silicate, aluminate, hydroxide, sulphate and chloride
19	Magnesium oxide	Sodium silicate, fluoride, hydroxide
20	Magnesium oxide	Sodium silicate, cryolite, hydroxide
21	Magnesium carbonate	Sodium silicate, hydroxide
22	Magnesium oxide, calcium sulphate	Sodium silicate, cryolite, hydroxide
23	Magnesium oxide, calcium carbonate	Sodium silicate, hydroxide
24	Magnesium oxide, tri-calcium phosphate	Sodium silicate, hydroxide
25	Magnesium oxide, tri-calcium phosphate	Sodium silicate, aluminate, hydroxide

Tables 1 and 2 give the results of tests conducted in order to see if the sodium silicate was soluble in the presence of sodium hydroxide at boiler temperatures, in the absence of any solid. Thus the results presented in Table 1 show that when about 3.5 millimoles per liter of SiO_2 (about 200 parts per million SiO_2) was in solution at the beginning of the tests, there was no marked change in concentration due to the temperature. In Table 2 the results of the introduction of sodium aluminate, along with the silicate and sodium hydroxide, are given. The silica and the aluminate both remained in solution at the higher temperatures.

(a) *Effect of Calcium Sulphate in Excess.*—Solutions containing sodium silicate and sodium hydroxide were added to an excess of solid calcium sulphate. The results of these tests are given in Table 3. These results show that, when there is sodium hydroxide present, the silica is removed from solution by the calcium sulphate, so that the resulting silica content is below 0.20 millimole per liter. In the absence of the hydroxide, the silica in solution increases.

(b) *Effect of Calcium Carbonate in Excess.*—The presence of calcium carbonate in contact with a solution containing sodium silicate and sodium hydroxide had no effect on the silica content in the solution (Table 4). When sodium aluminate was introduced along

TABLE 1

HYDROXIDE AND SILICA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED WITH NO SOLID PRESENT

Test No.	Temperature deg. F.	At End of Test		Added SiO_2
		OH	SiO_2	
		millimoles per liter		
535	470	13.8	2.5	3.7
		32.2	3.0	3.7
		28.7	1.9	3.7
		48.8	2.7	3.7
		48.0	2.5	3.7
540	470	15.8	3.5	3.3
		16.2	4.2	3.3
		33.3	5.0	3.3
		32.7	4.3	3.3
		53.4	4.8	3.3
		52.1	4.4	3.3

TABLE 2

HYDROXIDE, SILICA, AND ALUMINA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, ALUMINATE, AND HYDROXIDE HEATED WITH NO SOLID PRESENT

Test No.	Temperature deg. F.	At End of Test			Added	
		OH	SiO_2	Al_2O_3	SiO_2	Al_2O_3
		millimoles per liter				
549	470	16.4	2.4	0.41	4.3	0.50
		16.7	3.1	0.42	4.3	0.50
		31.9	3.2	0.46	4.3	1.00
		31.0	3.2	0.75	4.3	1.00
		51.3	3.3	1.44	4.3	1.50
		49.3	3.4	1.32	4.3	1.50

with the silicate (Table 5), the calcium carbonate had no effect on the silicate or aluminate content. When solutions containing silicate hydroxide and fluoride were heated in contact with calcium carbonate there was no appreciable change in the silica content of the solution (Table 6).

The introduction of cryolite, along with the sodium silicate and sodium hydroxide, when in contact with calcium carbonate, had no marked effect on the silica content of the solution (Table 7).

(c) *Effect of Calcium Fluoride in Excess.*—Table 8 gives the results of tests run to study the effect of calcium fluoride as a solid, when in contact with solutions containing sodium silicate and sodium

TABLE 3

HYDROXIDE, SILICA, AND SULPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED IN CONTACT WITH SOLID CALCIUM SULPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added SiO_2
		OH	SiO_2	SO_4	
		millimoles per liter			
505	360	0	0.31	3.50	4.6
		0	0.25	3.53	4.6
		0	0.79	4.92	4.6
		0	0.56	4.28	4.6
		1.1	0.18	6.56	4.6
		1.1	0.15	5.73	4.6
523	360	5.4	0.10	7.62	3.0
		12.5	0.09	9.12	3.0
		24.5	0.09	11.55	3.0
502	405	0	0.48	2.78	4.1
		0	0.75	2.64	4.1
		0.5	0.11	6.00	4.1
		0.6	0.20	5.55	4.1
521	405	5.3	0.12	7.05	3.7
		12.3	0.13	8.23	3.7
		22.6	0.10	11.20	3.7
507	470	0	0.25	2.2	4.1
		0	0.45	3.9	4.1
		3.4	0.19	7.2	4.1
		3.4	0.18	6.0	4.1
522	470	5.1	0.10	6.98	3.6
		13.2	0.09	8.55	3.6
		24.8	0.08	11.78	3.6
		23.9	0.08	12.20	3.6
504	540	0	0.17	1.32	4.0
		0	0.54	2.23	4.0
		0	0.64	3.92	4.0
		0.8	0.09	4.27	4.0
		1.0	0.08	8.10	4.0
508	540	4.7	0.11	6.60	3.8
		13.1	0.07	8.90	3.8
		23.4	0.09	11.75	3.8
		22.4	0.08	12.20	3.8

hydroxide. These results show that the silica content was not reduced to any marked extent.

(d) *Effect of Tri-calcium Phosphate in Excess.*—When solutions containing sodium silicate and sodium hydroxide were heated in contact with solid tri-calcium phosphate, the silica content of the solution was not reduced (Table 9).

The addition of sodium aluminate to the silicate and hydroxide solutions in contact with tri-calcium phosphate had no effect on the removal of the silicate, and the aluminate remained in solution (Table 10).

TABLE 4

HYDROXIDE AND SILICA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test		Added SiO_2
		OH	SiO_2	
		millimoles per liter		
509	360	4.6	3.9	4.7
		3.7	4.4	4.7
		7.0	4.8	4.7
		9.0	4.2	4.7
		15.1	4.1	4.7
		15.3	3.8	4.7
510	405	4.8	3.7	4.7
		3.8	3.9	4.7
		8.9	3.4	4.7
		9.4	4.0	4.7
		15.6	3.6	4.7
		14.5	3.0	4.7
517	470	3.3	2.4	3.5
		2.8	2.6	3.5
		7.4	2.2	3.5
		8.7	2.7	3.5
		13.5	3.0	3.5
		13.0	2.4	3.5
512	540	0.9	2.7	3.5
		1.6	2.3	3.5
		5.6	4.8	3.5
		6.7	4.7	3.5
		10.5	3.7	3.5
		10.6	3.5	3.5

TABLE 5

HYDROXIDE, SILICA, AND ALUMINA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND ALUMINATE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		OH	SiO_2	Al_2O_3	SiO_2	Al_2O_3
		millimoles per liter				
568	360	16.5	4.6	0.50	3.0	0.25
		16.7	4.0	0.62	3.0	0.25
		21.8	2.4	0.55	3.0	0.50
		26.0	3.1	0.70	3.0	0.50
		47.7	3.1	0.90	3.0	0.75
		49.0	3.4	0.95	3.0	0.75

The presence of either sodium fluoride or cryolite, along with sodium silicate and sodium hydroxide, when in contact with tricalcium phosphate, had no marked effect on the silica content of the solution (Tables 11 and 12).

TABLE 6

HYDROXIDE AND SILICA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, HYDROXIDE, AND FLUORIDE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test		Added	
		OH	SiO_2	SiO_2	F
		millimoles per liter			
525.....	470	13.7	2.4	3.6	8.9
		13.0	1.9	3.6	8.9
		23.7	3.3	3.6	8.9
		23.5	2.4	3.6	8.9
		39.6	2.4	3.6	8.9
		40.1	2.2	3.6	8.9

TABLE 7

HYDROXIDE, SILICA, ALUMINA, AND FLUORIDE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE AND CRYOLITE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added	
		OH	SiO_2	Al_2O_3	F	SiO_2	F
		millimoles per liter					
569.....	360	5.4	2.5	0.46	5.0	3.8	8.0
		6.0	2.9	0.38	4.2	3.8	8.0
		11.2	3.0	0.45	8.5	3.8	16.1
		14.1	1.9	1.12	9.8	3.8	24.1
		15.4	3.5	1.23	10.7	3.8	24.1

TABLE 8

HYDROXIDE AND SILICA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE HEATED IN CONTACT WITH SOLID CALCIUM FLUORIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test		Added SiO_2
		OH	SiO_2	
		millimoles per liter		
524.....	405	14.6	2.8	3.6
		15.3	2.9	3.6
		21.5	2.4	3.6
		23.3	2.7	3.6
		40.6	2.8	3.6
		40.0	2.9	3.6

TABLE 9

HYDROXIDE, SILICA, AND PHOSPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED IN CONTACT WITH SOLID TRI-CALCIUM PHOSPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added SiO_2
		OH	SiO_2	PO_4	
		millimoles per liter			
513	360	2.1	2.7	0.18	3.5
		12.1	3.9	0.23	3.5
		11.0	3.6	0.22	3.5
		19.2	3.5	....	3.5
520	360	14.9	4.3	0.16	3.9
		22.1	3.6	0.14	3.9
		21.9	3.7	0.14	3.9
		44.8	4.1	0.18	3.9
		40.0	3.9	0.13	3.9
514	405	2.7	3.4	0.17	3.6
		2.7	3.6	0.18	3.6
		7.7	3.5	0.21	3.6
		6.8	3.8	0.21	3.6
		11.3	3.9	0.19	3.6
		11.0	3.8	0.21	3.6
515	470	2.5	3.5	0.18	3.6
		6.6	3.7	0.17	3.6
		12.1	3.7	0.18	3.6
		12.3	3.6	0.15	3.6
518	470	15.1	5.3	0.14	3.5
		13.5	4.4	0.17	3.5
		25.7	4.4	0.18	3.5
		23.9	4.6	0.16	3.5
		41.2	4.5	0.17	3.5
		40.4	3.7	0.17	3.5

TABLE 10

HYDROXIDE, SILICA, ALUMINA, AND PHOSPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, HYDROXIDE, AND ALUMINATE HEATED IN CONTACT WITH SOLID TRI-CALCIUM PHOSPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added	
		OH	SiO_2	Al_2O_3	PO_4	SiO_2	Al_2O_3
		millimoles per liter					
563	360	14.5	2.7	0.58	0.20	3.3	0.50
		14.7	2.8	0.54	0.30	3.3	0.50
		32.0	2.9	0.76	0.25	3.3	1.00
		49.4	3.2	1.08	0.24	3.3	1.50

TABLE 11

HYDROXIDE, SILICA, AND PHOSPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, FLUORIDE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID TRI-CALCIUM PHOSPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		OH	SiO_2	PO_4	SiO_2	F
		millimoles per liter				
526.....	360	18.2	4.1	0.01	3.6	8.9
		18.5	3.8	0.01	3.6	8.9
		28.8	3.4	0.01	3.6	8.9
		29.8	4.2	0.01	3.6	8.9
		46.3	4.1	0.01	3.6	8.9
		45.5	3.7	0.01	3.6	8.9

TABLE 12

HYDROXIDE, SILICA, ALUMINA, FLUORIDE, AND PHOSPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE AND CRYOLITE HEATED IN CONTACT WITH SOLID TRI-CALCIUM PHOSPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test					Added	
		OH	SiO_2	Al_2O_3	F	PO_4	SiO_2	F
		millimoles per liter						
564.....	360	2.2	0.9	0.50	1.4	0.15	3.3	8.0
		7.1	2.2	0.35	4.2	0.15	3.3	8.0
		9.0	1.7	0.54	5.7	0.13	3.3	16.1
		11.8	2.7	0.53	5.7	0.10	3.3	16.1
		16.7	3.0	0.74	10.7	0.17	3.3	24.1
		16.2	2.8	0.60	12.5	0.08	3.3	24.1

(e) *Effect of Magnesium Oxide in Excess.*—Table 13 gives the results of tests conducted to study the influence of magnesium oxide in contact with solutions of sodium silicate and sodium hydroxide. The silica content was reduced to a figure below 0.10 millimole per liter (6 parts per million SiO_2) in the majority of the tests. The silica remained at this low figure, with the hydroxide varying between 1.0 and 40 millimoles per liter (40 and 1600 parts per million NaOH). These results indicate that magnesium oxide is very effective in removing silica from solution. The introduction of sodium sulphate, along with the silicate and hydroxide, had no retarding influence on the ability of the magnesium oxide to remove the silica from solution (Table 14). When chloride was also introduced (Table 15), the silica content was still reduced to a low amount.

TABLE 13

HYDROXIDE AND SILICA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test		Added SiO_2
		OH	SiO_2	
		millimoles per liter		
570	360	1.1	0.08	4.3
		2.7	0.08	4.3
		11.2	0.08	4.3
		26.8	0.14	4.3
		28.4	0.15	4.3
536	470	4.9	0.10	4.2
		11.1	0.07	4.2
		26.1	0.07	4.2
		25.8	0.05	4.2
		45.3	0.08	4.2
		43.9	0.07	4.2
574	540	2.3	0.08	4.3
		3.3	0.07	4.3
		12.4	0.11	4.3
		10.6	0.11	4.3
		28.1	0.30	4.3

TABLE 14

HYDROXIDE, SILICA, AND SULPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, SULPHATE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		OH	SiO_2	SO_4	SiO_2	SO_4
		millimoles per liter				
558	360	3.7	0.10	1.4	4.2	1.3
		3.5	0.10	1.3	4.2	1.3
		2.2	0.07	3.4	4.2	3.3
		2.5	0.08	6.5	4.2	6.7

When sodium aluminate, sodium silicate and sodium hydroxide were present in the solution in contact with magnesium oxide (Table 16), the silica was reduced to less than 0.05 millimole per liter (3 parts per million SiO_2), and the aluminate content was also reduced. The presence of aluminate in solution reduced the silica to a lower amount (see tests 551, 576, Table 16).

The presence of the sulphate and chloride along with the aluminate had no retarding effect on the ability of the magnesium oxide to remove the silica from solution (Tables 17 and 18).

TABLE 15

HYDROXIDE, SILICA, SULPHATE, AND CHLORIDE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, SULPHATE, CHLORIDE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added		
		OH	SiO_2	SO_4	Cl	SiO_2	SO_4	Cl
		millimoles per liter						
560.....	360	3.4	0.05	1.6	1.3	4.1	1.3	0.8
		3.7	0.06	1.4	1.3	4.1	1.3	0.8
		2.9	0.05	3.3	2.1	4.1	3.3	1.7
		2.3	0.05	3.4	2.5	4.1	3.3	1.7
		2.2	0.04	6.3	3.0	4.1	6.7	2.6
		3.8	0.04	6.6	3.0	4.1	6.7	2.6

When either sodium fluoride or cryolite was present, the magnesium oxide still removed the silica content of sodium silicate and sodium hydroxide solutions (Tables 19 and 20).

(f) *Effect of Magnesium Carbonate in Excess.*—Table 21 gives the results of tests conducted with magnesium carbonate in contact with solutions containing sodium silicate and sodium hydroxide. The silica content was reduced to a very low amount (0.05 millimole per liter, or 3 parts per million SiO_2).

(g) *Effect of Magnesium Oxide and Calcium Sulphate in Excess.*—Solutions containing sodium silicate, sodium aluminate, sodium fluoride, and sodium sulphate were tested in contact with both solid magnesium oxide and calcium sulphate (Table 22). The silica content was still reduced to a very low amount.

(h) *Effect of Magnesium Oxide and Calcium Carbonate in Excess.*—The presence of calcium carbonate had no retarding effect on the action of magnesium oxide in removing silica from solution (Table 23).

(i) *Effect of Magnesium Oxide and Tri-calcium Phosphate in Excess.*—The presence of tri-calcium phosphate had no retarding effect on the action of magnesium oxide in removing silica from solution (Tables 24 and 25).

(j) *Conclusions.*—The summary of conclusions which may be drawn from the results of the solubility tests is as follows:

(1) Calcium carbonate, calcium fluoride, and tri-calcium phosphate, when present as solids, do not react to reduce the silica content of alkaline sodium silicate solutions containing about 200 parts per million of SiO_2.

TABLE 16

HYDROXIDE, SILICA, AND ALUMINA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, ALUMINATE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		OH	SiO_2	Al_2O_3	SiO_2	Al_2O_3
		millimoles per liter				
594	360	1.3	0.03	0.23	4.4	1.76
		1.6	0.04	0.16	4.4	1.76
		6.2	0.04	0.17	4.4	3.52
		6.4	0.04	0.27	4.4	3.52
		10.8	0.04	0.29	4.4	5.28
583	360	4.5	0.05	0.43	4.3	1.80
		4.6	0.04	0.54	4.3	1.80
		13.6	0.06	0.44	4.3	3.60
		16.0	0.05	0.28	4.3	3.60
		22.0	0.06	1.22	4.3	5.40
		25.4	0.05	1.38	4.3	5.40
576	360	17.8	0.04	0.17	4.2	1.92
		17.0	0.04	0.14	4.2	1.92
		32.0	0.08	0.80	4.2	3.84
		36.0	0.04	0.74	4.2	3.84
		54.0	0.04	2.20	4.2	5.76
		56.2	0.04	2.24	4.2	5.76
551	360	13.7	0.20	0.19	3.3	0.50
		15.1	0.10	0.19	3.3	0.50
		31.6	0.16	0.18	3.3	1.00
		30.3	0.12	0.24	3.3	1.00
		48.3	0.16	0.24	3.3	1.50
		47.6	0.12	0.22	3.3	1.50
595	470	0.2	0.03	0.22	4.4	1.76
		0.2	0.04	0.21	4.4	1.76
		2.9	0.03	0.26	4.4	3.53
		4.6	0.03	0.46	4.4	3.53
		8.1	0.03	1.12	4.4	5.29
		5.9	0.04	1.09	4.4	5.29
582	470	5.8	0.02	0.30	4.4	1.93
		7.6	0.06	0.30	4.4	1.93
		14.1	0.05	0.95	4.4	3.87
		13.5	0.04	0.85	4.4	3.87
		21.3	0.05	1.90	4.4	5.80
		21.1	0.06	1.92	4.4	5.80
573	540	8.7	0.02	0.19	4.3	0.50
		13.5	0.07	0.24	4.3	0.50
		18.6	0.08	0.36	4.3	1.00
		31.0	0.08	0.23	4.3	1.00
		42.0	0.08	0.53	4.3	1.50
		45.8	0.08	0.50	4.3	1.50
596	540	0.0	0.03	0.0	3.9	1.98
		1.4	0.02	0.14	3.9	3.97
		2.9	0.02	0.18	3.9	3.97
		4.4	0.02	0.97	3.9	5.95
584	540	6.2	0.03	0.33	4.3	1.90
		6.3	0.03	0.32	4.3	1.90
		8.8	0.03	1.31	4.3	3.80
		13.6	0.04	1.04	4.3	3.80
		22.1	0.03	2.36	4.3	5.70
		20.8	0.05	2.71	4.3	5.70

TABLE 17

HYDROXIDE, SILICA, ALUMINA, AND SULPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, ALUMINATE, SULPHATE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added		
		OH	SiO_2	Al_2O_3	SO_4	SiO_2	Al_2O_3	SO_4
		millimoles per liter						
559.....	360	55.3	0.08	0.35	1.4	4.2	1.37	1.2
		54.6	0.07	0.34	1.5	4.2	1.37	1.2
		55.5	0.07	0.28	3.5	4.2	1.37	3.1
		55.0	0.06	0.37	6.6	4.2	1.37	6.3

TABLE 18

HYDROXIDE, SILICA, ALUMINA, SULPHATE, AND CHLORIDE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, ALUMINATE, SULPHATE, CHLORIDE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test					Added			
		OH	SiO_2	Al_2O_3	SO_4	Cl	SiO_2	Al_2O_3	SO_4	Cl
		millimoles per liter								
561.....	360	52.5	0.07	0.35	1.5	1.3	4.2	1.62	1.3	1.0
		56.0	0.06	0.34	1.5	1.1	4.2	1.62	1.3	1.0
		54.8	0.08	0.36	3.4	2.2	4.2	1.62	3.2	1.8
		55.3	0.07	0.35	3.3	2.2	4.2	1.62	3.2	1.8
		56.0	0.07	0.18	6.9	3.0	4.2	1.62	6.5	2.8
		56.2	0.08	0.27	6.6	3.0	4.2	1.62	6.5	2.8

TABLE 19

HYDROXIDE, SILICA, AND FLUORIDE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, FLUORIDE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		OH	SiO_2	F	SiO_2	F
		millimoles per liter				
545.....	470	18.1	0.21	21.6	4.4	17.8
		18.2	0.16	19.4	4.4	17.8
		33.6	0.20	17.4	4.4	17.8
		19.2	0.16	19.0	4.4	17.8
		46.6	0.20	22.6	4.4	17.8
		50.0	0.32	18.6	4.4	17.8

TABLE 20

HYDROXIDE, SILICA, ALUMINA, AND FLUORIDE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE AND CRYOLITE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added	
		OH	SiO_2	Al_2O_3	F	SiO_2	F
		millimoles per liter					
562	360	4.7	0.05	0.20	3.7	2.5	8.0
		5.2	0.06	0.21	3.6	2.5	8.0
		10.8	0.05	0.22	11.7	2.5	16.1
		10.5	0.09	0.21	10.5	2.5	16.1
		16.2	0.07	0.27	7.1	2.5	24.1
		16.1	0.06	0.45	7.1	2.5	24.1
567	470	5.6	0.04	0.30	8.9	4.1	7.5
		5.6	0.03	0.24	9.0	4.1	7.5
		11.1	0.06	0.21	12.7	4.1	15.0
		16.7	0.07	0.43	19.4	4.1	22.5
		17.0	0.06	0.43	19.6	4.1	22.5
571	540	4.5	0.04	0.20	3.7	4.1	7.1
		4.5	0.06	0.11	4.1	4.1	7.1
		9.9	0.07	0.27	8.1	4.1	14.2
		17.7	0.07	0.25	8.2	4.1	21.3
		17.6	0.08	0.28	9.0	4.1	21.3

TABLE 21

HYDROXIDE, SILICA, AND MAGNESIUM CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added SiO_2
		OH	SiO_2	Mg	
		millimoles per liter			
581	540	0	0.04	0.33	4.3
		0	0.04	0.21	4.3
		0	0.05	0.60	4.3
		0	0.04	0.32	4.3
		9.7	0.08	0.19	4.3

(2) Calcium sulphate, when present as a solid, reacts with alkaline sodium silicate solutions to reduce the silica content to 0.20 millimole per liter (12 parts per million SiO_2).

(3) Both magnesium oxide and magnesium carbonate, when present in excess, react with alkaline sodium silicate solutions to reduce the silica content to 0.10 millimole per liter (6 parts per million SiO_2),

TABLE 22

HYDROXIDE, SILICA, ALUMINA, FLUORIDE, AND SULPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE AND CRYOLITE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE AND CALCIUM SULPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test					Added	
		OH	SiO_2	Al_2O_3	F	SO_4	SiO_2	F
		millimoles per liter						
565.....	360	3.2	0.02	0.25	1.3	5.8	3.3	8.0
		0.8	0.03	0.19	1.3	5.6	3.3	8.0
		2.8	0.02	0.16	1.3	10.5	3.3	16.1
		3.0	0.01	0.22	1.2	10.4	3.	16.1
		7.4	0.02	0.24	1.4	13.3	3.3	24.1
		8.2	0.02	0.22	1.5	13.1	3.3	24.1
556.....	360	0.4	0.02	0.20	1.3	5.0	3.3	8.0
		1.3	0.03	0.16	1.2	5.5	3.3	8.0
		2.7	0.02	0.16	1.5	10.1	3.3	16.1
		7.1	0.01	0.24	1.9	13.7	3.3	24.1
566.....	470	1.1	0.04	0.07	1.8	5.0	3.9	8.0
		1.3	0.05	0.20	1.9	4.9	3.9	8.0
		4.0	0.05	0.19	2.4	9.2	3.9	16.1
		0.2	0.08	0.43	1.0	4.1	3.9	16.1
		7.5	0.04	0.32	2.4	13.2	3.9	24.1
		6.4	0.07	0.31	2.6	13.2	3.9	24.1
572.....	540	1.4	0.06	0.60	2.6	4.6	4.3	6.3
		2.0	0.03	0.09	3.0	4.6	4.3	6.3
		3.9	0.07	0.19	3.0	8.5	4.3	12.5
		4.0	0.07	0.26	2.9	8.6	4.3	12.5
		7.4	0.07	0.35	3.0	12.4	4.3	18.8
		8.1	0.07	0.24	3.2	12.3	4.3	18.8

TABLE 23

HYDROXIDE AND SILICA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE AND CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test		Added SiO_2
		OH	SiO_2	
		millimoles per liter		
531.....	470	4.4	0.05	3.8
		12.5	0.06	3.8
		27.6	0.09	3.8
		43.5	0.13	3.8

when the sodium hydroxide content is between 40 and 1600 parts per million.

(4) If sodium aluminate is present in amounts greater than 0.20 millimole per liter, and the sodium hydroxide content is between 40 and 2000 parts per million, magnesium oxide will reduce the silica

TABLE 24

HYDROXIDE AND SILICA CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE AND TRI-CALCIUM PHOSPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test		Added SiO_2
		OH	SiO_2	
		millimoles per liter		
532	470	8.3	0.12	3.8
		10.5	0.13	3.8
		24.5	0.13	3.8
		26.3	0.12	3.8
		36.2	0.16	3.8

TABLE 25

HYDROXIDE, SILICA, ALUMINA, AND PHOSPHATE CONTENT OF SOLUTIONS CONTAINING SODIUM SILICATE, ALUMINATE, AND HYDROXIDE HEATED IN CONTACT WITH SOLID MAGNESIUM OXIDE AND TRI-CALCIUM PHOSPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added	
		OH	SiO_2	Al_2O_3	PO_4	SiO_2	Al_2O_3
		millimoles per liter					
577	540	14.3	0.07	0.24	0.01	4.3	0.50
		14.1	0.07	0.18	0.01	4.3	0.50
		33.0	0.10	0.47	0.02	4.3	1.00
		20.0	0.10	0.27	0.02	4.3	1.00
		49.4	0.12	0.75	0.01	4.3	1.50
		48.5	0.11	0.49	0.02	4.3	1.50

content of alkaline sodium silicate solutions to 0.05 millimole per liter (3 parts per million SiO_2).

(B) Formation of Solid Silicates

In attempting to prevent silica scale, it is essential to have available data relative to the type of silica compounds which form in a boiler. Very little data of this nature are available, and, therefore, a study has been made to determine what these compounds might be.

The procedure followed in forming the desired solids was to mix the necessary amounts of the various chemicals together in water, place in the larger bomb (used in the solubility tests), and heat to the desired temperature. The sampling tube and filter inside the bomb were left out, and a fine copper gauze put inside of the top. At the end of the heating, the bombs were removed from the furnace,

TABLE 26
COMPOSITION OF ANALCITE, NATURAL AND SYNTHETIC

	Natural Analcite	Synthetic Analcite	
		Sample No. 12	Sample No. 23
SiO_2, per cent	54.4	52.7	54.2
Al_2O_3, per cent	23.3	24.5	24.6
Na_2O (difference), per cent	14.1	14.4	13.1
H_2O, per cent	8.2	8.2	8.1

inverted, and the sampling valve opened, thus allowing the liquid to be forced out and leave the solid behind in the bomb. When the bombs were cool, the solid was removed, washed with a little water, and dried.

(a) *Analcite*, $Na_2OAl_2O_3\ 4SiO_2\ 2H_2O$.—Since analcite has been found in boiler scales and has been synthesized, it was thought profitable to duplicate such a test. A solution of sodium silicate was used in which 70 cc. contained 10.8 grams of silica and 8 grams of 93.5-per cent solid sodium aluminate (equivalent to 4.6 grams of Al_2O_3). Mixtures of like composition were placed in six bombs. Water was added to the bombs containing sample numbers 7 and 8, so that the total volume was 110 cc.; the total volume of samples 9 and 10 was 180 cc.; the bombs containing samples 11 and 12 had a total volume of 330 cc. After heating the sealed bombs for 46 hours, they were sampled in the manner described.

It was found that samples 11 and 12 were of rather high purity and were much larger in size than the other samples. Petrographic examination* showed that the crystals were analcite in uniform rounded grains about 0.1 mm. in diameter. Chemical analysis (Table 26) showed that the crystals had almost identical composition with natural analcite.

A photomicrograph of sample number 12 at 35 magnifications is shown in Figure 1. The crystals are very hard and, when in a group, can be separated by pressing with a flat surface. The crystals themselves are not easily broken.

Figure 2 shows another photomicrograph (at 35 magnifications) of a later attempt (sample 23) to synthesize more analcite. The same conditions were used, except that the sodium aluminate was increased to 10 grams and 88 cc. of sodium silicate was used, with a total

*Petrographic examinations were made by Dr. R. E. Grim, Petrographer, Illinois State Geological Survey, Urbana, Illinois.

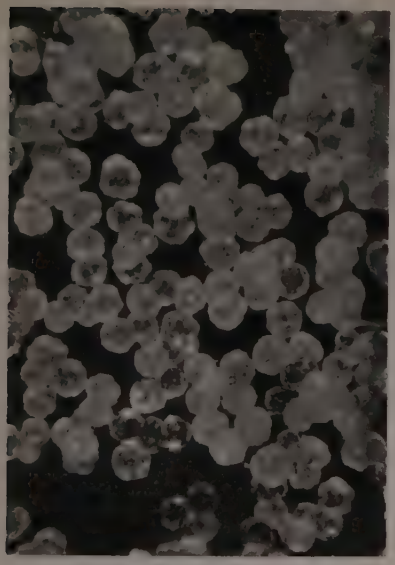


FIG. 1. PHOTOMICROGRAPH OF ANALCITE (SAMPLE 12)
35 x

FIG. 2. PHOTOMICROGRAPH OF ANALCITE (SAMPLE 23)
35 x

volume of 400 cc. The general crystalline form is the same as that of sample 12, and the analysis, as given in Table 26, showed the similarity to the natural analcite. Petrographic examination showed that the crystals were rounded grains of analcite, having a diameter of 0.02 mm. or less, with a few particles about 1 micron in diameter which were noncrystalline and too small for positive identification.

This sample was used later for a solubility study at various temperatures.

(b) *Magnesium Alumino Silicates in Presence of Sodium Hydroxide.*—A series of tests was run to make the following compounds: $MgO\ Al_2O_3\ SiO_2$, $MgO\ Al_2O_3\ 2SiO_2$, $MgO\ Al_2O_3\ 3SiO_2$, and $MgO\ Al_2O_3\ 4SiO_2$ (samples numbered 13, 15, 26, and 18 respectively). These were made from magnesium oxide, sodium aluminate, and sodium silicate solutions. The proper amounts of each of the constituents were used to give a theoretical yield of 10 grams.

The solid magnesium oxide and sodium aluminate were stirred into a volume of water in the bomb, and the sodium silicate was added with constant stirring. The total volume of the mixture was approximately 350 cc. After heating for two days at 540 deg. F., the bombs were sampled and the solid analyzed. The results of the chemical analysis are given in Table 27.

TABLE 27

COMPOSITION OF SOLIDS FORMED FROM MAGNESIUM OXIDE, SODIUM ALUMINATE, AND SODIUM SILICATE AT 540 DEG. F.

	Sample 13	Sample 15	Sample 26	Sample 18
MgO, per cent	8.59	8.32	6.58	7.4
Al_2O_3, per cent	40.8	31.4	28.8	23.4
SiO_2, per cent	31.7	40.6	46.6	52.0
H_2O, per cent	13.25	8.0	8.84	8.97
Not determined, per cent	5.7	11.7	9.2	8.3

From the results given in Table 27, the formula for sample 13 seems to be $MgO\ 1.9Al_2O_3\ 2.5SiO_2\ 3.5H_2O$, and not $MgO\ Al_2O_3\ SiO_2$, as anticipated from the ratios of the constituents placed in the bomb. Figure 3, a photomicrograph at a magnification of 35, shows no crystalline form, and apparently no reaction had taken place between the constituents of the mixture.

Petrographic examination of this sample showed it to be "non-crystalline (glassy) particles ranging in size up to 0.03 mm. with an index of refraction ranging from 1.520 to 1.535.

"Published data for magnesium aluminum silicate glasses are too meager to be of much value. Quoted indices for anhydrous compounds range from 1.520 to 1.560, depending on the silica content of the original melt. Indices of hydrous materials would be lower in general than those of the anhydrous. These data suggest that the range of indices in the glass in this sample is due to a non-uniform distribution of silica. Hydrous silica has a much lower index, which would seem to eliminate the possibility that this sample is composed of a mixture of uncombined hydrous oxides."*

Figure 4 shows the solid formed in an attempt to make $MgO\ Al_2O_3\ 2SiO_2$ (sample 15) as described above. The chemical composition is given in Table 27, and the formula from this analysis seems to be $MgO\ 1.5Al_2O_3\ 3.3SiO_2\ 2.2H_2O$. The photomicrograph shows some glassy particles which were too small to be separated and analyzed. There were, nevertheless, no definite crystals formed in the reaction. Petrographic examination definitely showed these particles to be non-crystalline, having a diameter of about 1 micron and indices of refraction ranging from 1.535 to 1.555. The range of indices indicates non-uniform composition.

Sample 26 was the product formed in an attempt to make $MgO\ Al_2O_3\ 3SiO_2$. The composition of this sample is shown in Table 27.

*Footnote, page 26.

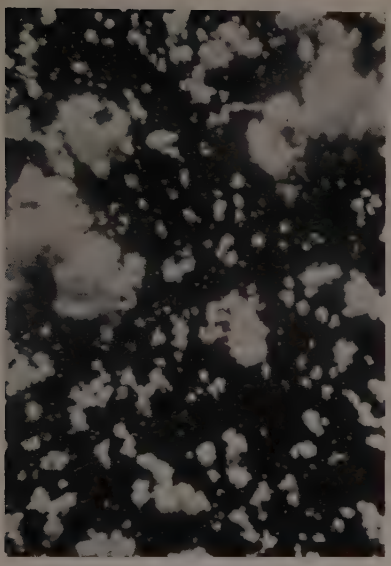


FIG. 3. PHOTOMICROGRAPH OF SAMPLE 13
35 x

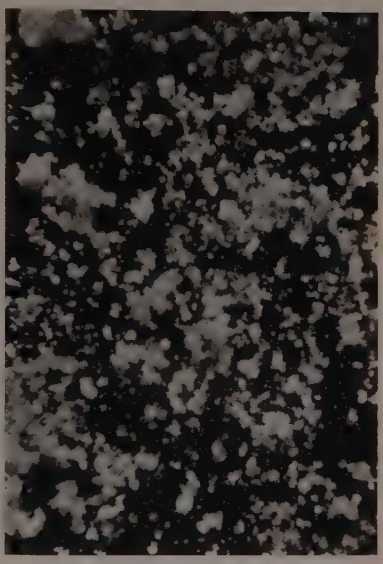


FIG. 4. PHOTOMICROGRAPH OF SAMPLE 15
35 x

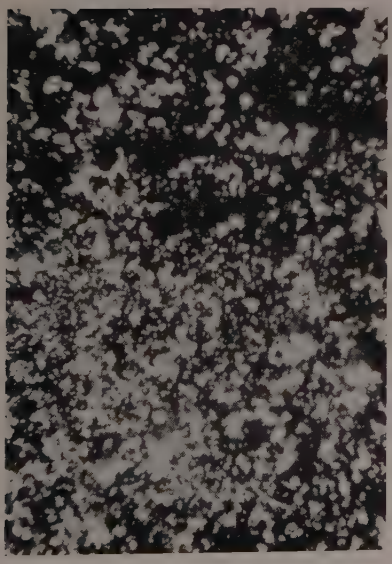


FIG. 5. PHOTOMICROGRAPH OF SAMPLE 26
35 x

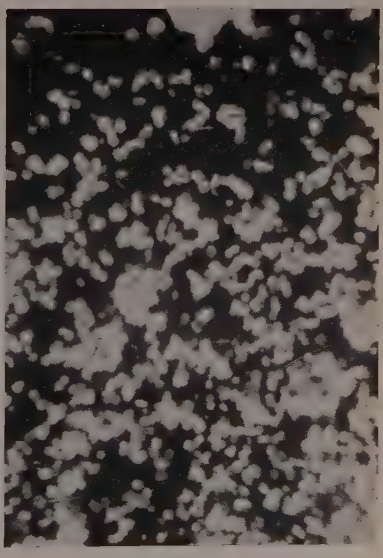


FIG. 6. PHOTOMICROGRAPH OF SAMPLE 18
35 x

The formula for this solid, according to this analysis, would be $MgO\ 2.8Al_2O_3\ 4.75SiO_2\ 3.2H_2O$. A study of Fig. 5 shows some small grains that may be crystalline, but are hard to identify merely by inspection. A petrographic study showed that these were small grains of analcite which had a diameter no larger than 0.06 mm., and irregular glossy particles with indices different from that of analcite (1.488 to 1.550). This may indicate that crystallization was just beginning to take place.

Amounts of magnesium oxide, sodium aluminate, and sodium silicate were mixed in proper ratio to form the $MgO\ Al_2O_3\ 4SiO_2$ (sample 18). Figure 6 is a photomicrograph of the solid formed, and from the analysis (given in Table 27) it seems to have the following formula: $MgO\ 1.25Al_2O_3\ 4.72SiO_2\ 2.7H_2O$.

It is very improbable that a compound would have such a molar relation between the constituents. Yet, from the photomicrograph of this solid, definite crystals can be seen which were impossible to identify by chemical analysis. Petrographic analysis made upon this sample showed that the crystals were "composed mainly of analcite in rounded grains, reaching 0.02 mm. in diameter. They also contained a few irregular glassy grains each 0.02 mm. in diameter, with an index varying in different grains from that of analcite (1.488 to 1.530)."*

The two tests (samples 26 and 18) last discussed indicate that analcite is formed in preference to a magnesium alumino silicate in the presence of sodium salts when the ratio of silica to alumina approaches four.

The solids formed in this set of tests were flocculent, and they settled in the container very rapidly after being shaken. This is a desirable feature for sludges that are formed in boilers.

(c) *Magnesium Silicates in Presence of Sodium Hydroxide.*—Two tests were run in an attempt to make a magnesium silicate in the presence of sodium hydroxide. Proper amounts of magnesium oxide and of sodium silicate solution were mixed in the bomb so as to give a yield of 20 grams of solid. Enough water was added to make the total volume about 350 cc.

Sample 27 was the result of an attempt to synthesize $MgO\ SiO_2$ at 540 deg. F. From the results of the chemical analysis given in Table 28, the compound actually formed should have the formula $MgO\ 1.2SiO_2\ 0.58H_2O$. When this solid was placed in water the solution was somewhat gelatinous, and did not settle as fast as one of

*Footnote, page 26.

FIG. 7. PHOTOMICROGRAPH OF SAMPLE 27
35 x

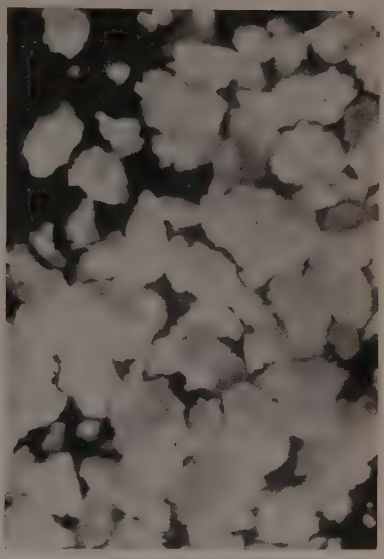


FIG. 8. PHOTOMICROGRAPH OF SAMPLE 29
35 x

the magnesium alumino silicates. After being dried, the solid was very hard and brittle.

Figure 7 shows this sample at 35 magnifications. No crystals had formed in this mass, and it appeared to be a mixture of the constituents added to the bomb.

Petrographic examination indicated that the particles were "in the initial stage of crystallization, showing development of crystallites enclosed in glass. Index of these particles varied from 1.535 to 1.550, which indicates unequal distribution of components. The index of refraction of anhydrous $MgOSiO_2$ glass is 1.5767. Hydrous material would have a lower value. The sample also contained a few irregular particles, at times showing faint crystallization, with an index of refraction reaching as low as 1.500. These may be particles of uncombined oxides."

Sample 29 was the result of an attempt to prepare MgO $2SiO_2$ at 540 deg. F. The results given in Table 28 indicate the formula of this solid to be MgO $1.8SiO_2$ $0.87H_2O$. This approaches the composition of the solid anticipated. In Fig. 8 the solid is shown at 35 magnifications, and it appears much like sample 27. Petrographic examination showed it to be similar to the sample previously discussed.

TABLE 28
COMPOSITION OF SILICATES FORMED FROM MAGNESIUM OXIDE AND SODIUM SILICATE AT 540 DEG. F.

	Sample 27	Sample 29
MgO, per cent	33.1	24.1
SiO_2, per cent	58.1	64.7
H_2O, per cent	10.3	9.23

TABLE 29
COMPOSITION OF SOLIDS FORMED FROM SILICIC ACID AND MAGNESIUM HYDROXIDE AT 540 DEG. F.

	Sample 32	Sample 34
MgO, per cent	34.1	26.2
SiO_2, per cent	51.0	66.7
H_2O, per cent	11.5	8.2

(d) *Magnesium Silicates in Absence of Sodium Hydroxide.*—To prepare samples of magnesium silicates in the absence of sodium hydroxide the silica was added as silicic acid and the magnesium as the hydroxide. Silicic acid was prepared by pouring sodium silicate (specific gravity 1.1) into an excess of 3 normal hydrochloric acid, and the sodium chloride formed was separated by dialyses through cellophane. This required about 40 hours of constant stirring, the wash water being changed frequently during this time. Magnesium hydroxide was prepared from magnesium sulphate by precipitation with ammonium hydroxide. Purification of the precipitate was accomplished by decantation and washing until no trace of sulphate was found in the wash water.

A mixture of the silicic acid and magnesium hydroxide was prepared so that the theoretical solid formed from this solution would be $MgO\ SiO_2$. By analysis (Table 29), however, it was found that this solid (sample 32) corresponded to the following formula: $MgO\ SiO_2\ 0.75H_2O$. The solid appeared very much like the sample shown in Fig. 9. Petrographic examination showed that the "bluish white material (somewhat transparent) of this sample was a glass with an index of refraction equal to 1.557. A few particles appearing faintly crystalline with an index of 1.530 were also present."

FIG. 9. PHOTOMICROGRAPH OF SAMPLE 34
35 x

MgO $2SiO_2$ was prepared by taking proper amounts of silicic acid and magnesium hydroxide, which were prepared as already described. Water was added to the mixture until the volume was about 250 cc. The composition of the solid formed (sample 34) is shown in Table 29. This mixture corresponded to the following formula: MgO $1.7SiO_2$ $0.71H_2O$. Figure 9 is a photomicrograph at 35 magnifications of this sample. Some of the transparent (glassy) matter was separated and analyzed. The composition of this was 92-per cent SiO_2, and 4.4-per cent MgO. The large egg-shaped particles appear to be pure MgO.

Petrographic examination of sample 34 showed it to be "composed of particles slightly crystallized with an index of refraction about equal to 1.550, and glassy particles showing no crystallization, in which the index ranges from 1.510 to 1.530." It seems probable that this sample was not completely mixed when it was placed in the bomb.

(e) *Conclusions.*—The summary of conclusions which may be drawn from the results of the study on the formation of solid silicates is as follows:

(1) Large crystals of analcite may be formed at 540 deg. F. from a solution containing 135 millimoles of alumina and 524 millimoles of silica per liter.

TABLE 30

SOLUBILITY OF ANALCITE IN WATER AND SODIUM HYDROXIDE FROM 360 TO 540 DEG. F.

Results recorded in millimoles per liter

Test No.	Temperature deg. F.	Added NaOH	Found in Solution				Ratio $\frac{SiO_2}{Al_2O_3}$
			NaOH	Na_2CO_3	Al_2O_3	SiO_2	
612–1	360	0	1.6	0.4	0.32	0.7	2.2
2		0	2.4	0.6	0.34	0.9	2.6
3		2.4	1.2	1.6	0.27	1.2	4.4
4		2.4	1.0	1.3	0.28	0.9	3.2
5		5.9	3.0	3.3	0.43	1.6	3.7
6		5.9	3.2	3.4	0.42	1.8	4.3
613–7	405	0	0.4	0.8	0.57	1.4	2.4
8		0	0.5	0.9	0.45	1.2	2.7
9		2.5	0.7	1.2	0.45	0.8	1.7
10		2.5	1.0	1.5	0.52	1.0	2.0
12		6.2	2.8	3.4	0.45	1.8	4.1
13		6.2	3.2	3.5	0.52	1.6	3.1
614–13	470	0	0.3	0.9	0.57	1.5	2.6
14		0	0.5	1.0	0.53	1.7	3.2
15		0.2	0.9	2.2	0.46	1.8	3.9
18		2.5	0.9	2.2	0.48	1.7	3.5
19		6.2	2.9	3.9	0.88	2.4	2.7
20		6.2	3.5	3.9	0.84	2.1	2.5
615–21	540	0	0.4	1.3	0.78	2.2	2.7
22		0	0.2	1.0	0.62	1.8	2.8
23		2.5	0.7	2.5	0.70	2.3	2.3
24		2.5	0.8	2.2	0.64	2.2	3.4
25		6.2	3.3	4.0	0.96	2.8	2.9
26		6.2	3.3	4.0	1.03	2.5	2.4

(2) Magnesium alumino silicate is formed in preference to analcite when the ratio of silica to alumina is less than four.

(3) When alumina is present, more flocculent sludges are formed.

(C) Solubility Studies of Silicates

(a) *Solubility of Analcite.*—To determine the solubility of analcite, tests were run at 360, 405, 470 and 540 deg. F., using the analcite (sample 23) formed in a previous experiment. It was estimated that only 0.8 gram of analcite would be required to have an excess present in the bomb after reaction. The solubility was studied in water and two different concentrations of sodium hydroxide, corresponding to 100 and 250 parts per million of sodium hydroxide. The results of this series of tests are shown in Table 30.

From these tests it is seen that the analcite is more soluble at higher temperatures, and slightly more soluble with increased alkalinity, but the solubility of SiO_2 and Al_2O_3 is not in the same ratio as combined in this complex silicate. Since the ratio of SiO_2 and Al_2O_3 is less than four, more Al_2O_3 is in solution than SiO_2. There is some silica that did not go into solution, and thus may have precipitated

TABLE 31

SOLUBILITY OF SODIUM ALUMINATE AND SODIUM SILICATE AT 360 TO 540 DEG. F.

Concentrations expressed in millimoles per liter

Test No.	Temperature deg. F.	Solution Added				Remaining in Solution				Loss		Ratio $\frac{\text{Loss } SiO_2}{Al_2O_3}$
		NaOH	Na_2CO_3	SiO_2	Al_2O_3	NaOH	Na_2CO_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3	
600– 7	360	27.4	16.1	6.9	2.1	23.8	15.6	5.9	1.3	1.05	0.8	1.2
8		27.4	16.1	6.9	2.1	22.3	14.2	4.8	0.7	2.06	1.4	1.4
9		54.8	32.2	13.9	4.3	48.5	29.6	7.5	1.9	6.40	2.3	2.7
10		54.8	32.2	13.9	4.3	47.7	30.2	11.6	3.1	2.30	1.1	1.9
11		82.2	48.3	20.8	6.4	76.9	44.5	8.7	2.1	12.07	4.3	2.7
12		82.2	48.3	20.8	6.4	74.0	43.1	7.8	1.7	12.97	4.7	2.7
601– 1	405	27.2	16.2	7.2	2.1	23.4	15.5	5.1	1.7	2.04	0.4	4.5
2		27.2	16.2	7.2	2.1	23.2	16.1	5.1	1.7	2.02	0.4	4.8
3		54.4	32.5	14.4	4.3	48.5	30.1	7.5	2.1	6.89	2.1	3.1
4		54.4	32.5	14.4	4.3	39.6	24.2	6.1	1.7	8.30	2.5	3.2
6		81.6	48.7	21.6	6.5	76.6	44.1	9.2	2.2	12.31	4.2	2.9
602–13	470	27.2	16.2	7.2	2.1	20.9	15.8	2.7	1.7	4.41	0.4	9.2
14		27.2	16.2	7.2	2.1	20.8	15.8	5.4	1.6	1.80	0.4	3.6
15		54.4	32.5	14.4	4.3	44.0	29.4	5.6	1.6	8.85	2.6	3.3
18		54.4	32.5	14.4	4.3	46.0	30.3	5.8	1.8	9.60	2.5	3.8
19		81.6	48.7	21.6	6.5	71.9	44.1	8.0	1.7	13.60	4.8	2.7
20		81.6	48.7	21.6	6.5	72.0	43.7	8.4	0.4	13.11	6.0	2.1
603–21	540	25.4	15.8	7.1	2.1	22.8	22.8	2.5	0.1	4.56	2.0	2.2
23		50.8	31.6	14.3	4.2	49.0	55.4	5.6	1.0	8.63	3.1	2.7
24		50.8	31.6	14.3	4.2	57.7	57.2	5.6	0.0	8.63	4.2	2.0
25		76.2	57.4	21.4	6.3	74.7	43.1	7.3	0.9	14.16	5.4	2.5
26		76.2	57.4	21.4	6.3	77.3	44.6	7.4	1.1	14.07	5.2	2.6

FIG. 10. PHOTOMICROGRAPH OF CRYSTALS FROM TEST 602-19
35 x

in the bomb. If the alkalinity had been much higher, it might have been possible to bring more silica into solution. These tests apparently indicate that analcite scale formation may be prevented if the silica does not exceed 3 millimoles per liter.

(b) *Reaction Between Sodium Silicate and Sodium Aluminate Solutions.*—A series of tests was run using sodium silicate and sodium aluminate in such proportions that the ratio of silica to alumina was about four at various concentrations and temperatures. The results of these tests are presented in Table 31; they indicate that more SiO_2 and Al_2O_3 are lost at higher temperatures and concentrations than at lower temperatures and concentrations. It will be noted, however, that the ratio of SiO_2 to Al_2O_3 lost approaches four only at the lower concentrations and at 405 and 470 deg. F. Apparently some other silicate that does not have the same composition as analcite was being formed.

The solids formed in these tests were removed from the bombs and inspected with a microscope. The amounts of the samples obtained were too small for chemical analysis. Much iron oxide was present with the crystals formed.

The photomicrograph shown in Fig. 10 shows the solid formed in test 602-19. These crystals do not appear to be analcite, as was formed in some previous tests (see Fig. 1) in which a much higher

TABLE 32

REACTION BETWEEN MAGNESIUM SULPHATE AND SODIUM SILICATE AT 360 AND 540 DEG. F.

Results expressed in millimoles per liter

Test No.	Temperature deg. F.	Solution Added			Remaining in Solution					Ratio of SiO_2 to MgO Lost
		NaOH	$MgSO_4$	Na_2SiO_3	NaOH	Na_2CO_3	MgO	SiO_2	SO_4	
624– 1	360	33.8	25.4	25.8	0	0.31	0.89	0.1	24.6	1.0
2		33.8	25.4	25.8	0	0.27	0.99	0.8	24.4	1.0
3		20.0	25.4	51.6	0	0.12	0.57	4.5	25.4	1.9
4		20.0	25.4	51.6	0	0.13	0.48	4.6	25.2	1.9
5		5.0	25.4	77.4	0	0.16	1.03	7.6	25.0	2.8
6		5.0	25.4	77.4	0	0.20	1.06	7.6	25.0	2.8
625–21	540	33.8	25.4	25.8	0	0.34	1.67	0.8	24.9	1.0
23		20.0	25.4	51.6	0	0.13	0.40	2.6	14.5	1.1
24		20.0	25.4	51.6	0	0.00	2.11	10.0	25.6	1.7
25		5.0	25.4	77.4	0	0.00	0.21	11.9	25.5	2.6
26		5.0	25.4	77.4	0	0.00	0.24	12.2	24.9	2.6

TABLE 33

COMPOSITION OF SOLIDS FORMED FROM MAGNESIUM SULPHATE AND SODIUM SILICATE AT 360 AND 540 DEG. F.

Test No.	Temperature deg. F.	Composition, per cent				Molar Ratios		
		MgO	SiO_2	H_2O	R_2O_3	MgO	SiO_2	H_2O
624– 1	360	31.6	47.6	17.1	6.1	1	1.0	1.2
2		30.6	47.9	16.2	6.4	1	1.0	1.1
3		22.7	59.0	12.9	8.8	1	1.7	1.2
4		20.6	55.5	11.1	7.4	1	1.8	1.2
5		16.0	63.2	11.6	8.9	1	2.6	1.6
6		15.3	66.0	13.9	5.8	1	2.8	2.0
625–21	540	26.4	49.7	15.3	4.5	1	1.3	1.4
22		32.1	49.7	15.3	5.3	1	1.0	1.0
23		23.2	59.9	9.2	11.2	1	1.7	0.8
24		22.2	59.4	8.8	9.8	1	1.8	0.8
25		18.6	69.3	6.0	5.1	1	2.4	0.7
26		13.7	67.0	7.8	12.0	1	3.3	1.2

concentration of sodium silicate and sodium aluminate was used. These crystals probably are a sodium alumino silicate complex with the ratio of SiO_2 to Al_2O_3 of about 2.7, interpreted from the SiO_2 and Al_2O_3 loss of the solution from which these crystals are formed.

(c) *Reaction Between Sodium Silicate and Magnesium Sulphate Solutions.*—Tests were run to determine if there is any reaction between sodium silicate and magnesium sulphate at 360 and 540 deg. F. An attempt was made also to determine the composition of the sludge that was formed during the reaction. Sodium silicate and magnesium sulphate were mixed in such proportions (in the bomb) that the ratios

of SiO_2 to MgO were 1 to 1, 2 to 1, and 3 to 1. Sodium hydroxide was added to the mixture, so that the solution would be alkaline after the reaction. It is obvious from Table 32 that not enough hydrate was added, that less silica and magnesium salt are removed from the solution at the higher temperature (540 deg. F.) than at the lower temperature, and that the ratio of the silica lost to the magnesium lost appears to be less at higher temperatures.

The composition of the solids formed is given in Table 33. It will be noticed that the ratio of the silica to magnesium in the solid is very much the same as calculated from the loss of these constituents from solution.

These solids contained much iron, due to the low alkalinity in the bombs, but this does not affect the calculations in determining the ratios. When in water the solids formed a somewhat gelatinous precipitate, which settled slowly. This form of solid probably would not make a good boiler sludge.

(d) *Reaction Between Sodium Silicate and Magnesium Sulphate Solutions with Solid Sodium Aluminate.*—To study the reaction of sodium silicate and magnesium sulphate with the sodium aluminate, mixtures were made so that the ratio of Al_2O_3 to MgO was 1 to 1 throughout the tests, and the ratio of SiO_2 to MgO was 1, 2, and 3 in the various bombs. These tests were run at 360 and 540 deg. F., with a duplicate of each sample.

The results of these tests, shown in Table 34, indicate that more magnesium was removed from solutions when the lower amounts of silica were added. From the same table, it will be noticed that the Al_2O_3 present is lower at the higher concentrations, showing that more alumina has reacted, but is not completely precipitated in any of the concentrations of magnesium salt or silicate used. Ratios of the loss of magnesium to loss of silica are very near the anticipated values, except in tests 627-25 and 627-26. In these tests the ratio is about 3.5 instead of 3 (molar ratio on the original solution). These solids are more flocculent than the solids formed without sodium aluminate.

The solids formed were analyzed as before, and the results are given in Table 35. The ratios of SiO_2 to MgO in this table and in the previous table do not check as closely as the ratios for these compounds given in Tables 32 and 33.

(e) *Reaction Between Sodium Silicate and Calcium Chloride Solution.*—Tests were run using a sodium silicate and calcium chloride mixture. Sodium hydroxide was added, in an attempt to have an alkaline solution at the completion of the reaction, but this was not

Table 34

Reaction Between Magnesium Sulphate, Sodium Silicate, and Sodium Aluminate at 360 and 540 deg. F.

(Solid added equivalent to 24.9 millimoles Al_2O_3 per liter)
Results given in millimoles per liter

Test No.	Temperature deg. F.	Solution Added			Remaining in Solution						Ratio of SiO_2 to MgO Lost
		NaOH	$MgSO_4$	Na_2SiO_3	NaOH	Na_2CO_3	MgO	SiO_2	Al_2O_3	SO_4	
626– 1	360	37.5	25.4	25.8	35.1	26.2	1.2	2.2	10.1	25.3	0.9
2		37.5	25.4	25.8	33.8	28.0	1.4	2.0	10.5	26.0	0.9
3		22.5	25.4	51.6	20.3	19.2	1.1	3.1	4.6	25.0	1.9
4		22.5	25.4	51.6	22.1	18.7	0.7	3.3	4.1	24.8	1.9
5		7.5	25.4	77.4	15.6	15.1	1.2	2.7	3.5	25.0	3.0
6		7.5	25.4	77.4	13.5	13.8	1.5	2.9	3.3	24.4	3.1
627–21	540	37.5	25.4	25.8	28.2	22.4	1.2	0.8	9.4	18.9	1.0
22		37.5	25.4	25.8	35.2	25.2	0.8	1.1	13.0	....	1.0
23		22.5	25.4	51.6	17.6	16.2	1.9	3.6	7.2	21.6	2.0
24		22.5	25.4	51.6	16.2	15.8	1.4	2.9	7.7	22.9	2.0
25		7.5	25.4	77.4	2.5	7.0	4.2	4.8	2.6	16.9	3.4
26		7.5	25.4	77.4	4.2	8.5	4.8	4.9	4.4	22.9	3.5

TABLE 35

COMPOSITION OF SOLID FORMED FROM MAGNESIUM SULPHATE, SODIUM SILICATE, AND SODIUM ALUMINATE AT 360 AND 540 DEG. F.

Test No.	Temperature deg. F.	Composition, per cent				Molar Ratios			
		MgO	SiO_2	Al_2O_3	H_2O	MgO	SiO_2	Al_2O_3	H_2O
626– 1.....	360	10.1	28.7	43.3	15.1	1	1.9	1.7	3.5
2.....		9.6	28.4	42.7	17.0	1	1.8	1.7	3.9
3.....		8.7	38.2	34.2	12.8	1	2.9	1.5	3.3
4.....		7.7	37.7	31.4	13.2	1	3.3	1.6	3.8
5.....		10.7	43.6	26.9	13.3	1	2.7	0.9	2.3
6.....		7.1	42.4	26.9	13.3	1	4.0	1.4	4.1
627–21.....	540	12.1	30.3	42.2	11.2	1	1.6	1.3	2.0
22.....		21.5	30.2	33.2	11.9	1	0.9	0.6	1.2
23.....		6.7	39.8	35.8	6.9	1	3.6	2.1	2.3
24.....		6.5	38.8	35.0	5.4	1	4.0	2.1	1.8
25.....		8.8	46.1	27.3	6.2	1	2.9	1.2	1.5
26.....		8.2	42.8	28.1	6.7	1	3.5	1.3	1.8

TABLE 36

REACTION BETWEEN CALCIUM CHLORIDE AND SODIUM SILICATE AT 360 AND 540 DEG. F.

Results expressed in millimoles per liter

Test No.	Temperature deg. F.	Solution Added			Remaining in Solution					Ratio of SiO_2 to CaO Lost
		NaOH	$CaCl_2$	Na_2SiO_3	NaOH	Na_2CO_3	CaO	SiO_2	Cl	
628– 7.....	360	37.5	28.4	25.8	0	0.38	2.5	0.2	56.4	0.9
8.....		37.5	28.4	25.8	0	0.20	2.6	0.3	56.7	0.9
9.....		22.5	28.4	51.6	0	0.12	2.5	4.8	57.2	1.8
10.....		22.5	28.4	51.6	0	0.75	2.4	4.5	56.5	1.8
11.....		7.5	28.4	77.4	0	0.19	2.4	5.1	57.3	2.7
12.....		7.5	28.4	77.4	0	0.25	2.6	5.9	57.5	2.7
629–21.....	540	37.5	28.4	25.8	0	0.18	2.5	0.9	55.9	0.9
22.....		37.5	28.4	25.8	0	0.17	2.2	0.9	55.6	0.9
23.....		22.5	28.4	51.6	0	0.31	2.5	3.6	56.7	1.8
24.....		22.5	28.4	51.6	0	0.32	2.7	3.7	61.6	1.8
25.....		7.5	28.4	77.4	0	0.27	2.3	14.8	56.4	2.4
26.....		7.5	28.4	77.4	0	0.22	1.9	16.7	56.7	2.2

accomplished, and the result was a high R_2O_3 content in the solids formed. The ratio of silica to calcium was 1, 2, and 3 for the various bombs at one temperature.

Results of these tests are shown in Table 36. The amount of calcium remaining in the solution is almost constant throughout the entire set of tests, but the amount of silica in solution is greater at the higher concentrations of silica and considerably greater at the higher temperatures. From this it would be expected that the ratios of silica to calcium would be less than the amounts added, as shown in Table 37.

TABLE 37
COMPOSITION OF SOLID FORMED FROM CALCIUM CHLORIDE AND SODIUM SILICATE AT 360 AND 540 DEG. F.

Test No.	Temperature deg. F.	Composition, per cent				Molar Ratios		
		CaO	SiO_2	H_2O	R_2O_3	CaO	SiO_2	H_2O
628– 7	360	42.1	44.2	3.0	6.7	1	0.9	0.2
8		33.2	45.1	7.3	12.2	1	1.2	0.6
9		31.0	58.9	8.0	1.4	1	1.7	0.8
10		27.5	57.6	9.3	3.7	1	1.9	1.0
11		20.0	65.5	7.9	4.9	1	3.0	1.2
12		19.8	66.5	7.9	5.1	1	3.0	1.2
629–21	540	45.5	46.9	6.1	2.9	1	0.9	0.4
22		40.3	46.1	6.2	...	1	1.0	0.4
23		23.4	57.6	6.4	10.7	1	2.3	0.8
24		25.9	59.4	6.0	5.8	1	2.1	0.7
25		25.4	73.2	5.9	3.9	1	2.7	0.7
26		23.6	65.7	5.8	6.1	1	2.6	0.7

From the results shown in Tables 36 and 37, it appears that the combining ratio of calcium and silica is about 3 at 360 deg. F., but at 540 deg. F. the combining ratio is about 2.5. This indicates that for higher temperatures more calcium must be present to remove silica. This is practically the same condition as found in the tests of magnesium sulphate and sodium silicate mixtures. The solutions obtained when calcium chloride was used were turbid after filtering, while the solutions obtained when magnesium sulphate was used were clear, except for a small amount of iron present.

(f) *Reaction Between Sodium Silicate and Calcium Chloride Solutions with Solid Sodium Aluminate.*—Tests of the reaction between sodium silicate and calcium chloride with sodium aluminate mixtures were made so that the ratio of Al_2O_3 to CaO was 1 to 1 throughout the tests, and the ratios of SiO_2 to CaO were 1, 2, and 3 in the various bombs. These tests were run at 360 and 540 deg. F., with a duplicate of each sample.

The results of these tests, shown in Table 38, indicate that at 540 deg. F. more calcium is removed than at 360 deg. F., and that less silica is removed at higher temperatures and concentrations. The sodium aluminate is more soluble in the solution containing less silica, but temperature does not have much effect on the solubility. The ratio of silica to calcium removed from solution is somewhat lower at the higher temperature, and is about 2.6 at the higher concentration instead of the anticipated ratio of three. The amount of calcium remaining in solution is less than the magnesium in solution in tests using magnesium instead of calcium with silica and alumina.

Table 38

Reaction Between Magnesium Sulphate, Sodium Silicate, and Sodium Aluminate at 360 and 540 deg. F.

(Solid added equivalent to 24.9 millimoles Al_2O_3 per liter)
Results given in millimoles per liter

Test No.	Temperature deg. F.	Solution Added			Remaining in Solution						Ratio of SiO_2 to CaO Lost
		NaOH	$CaCl_2$	Na_2SiO_3	NaOH	Na_2CO_3	CaO	SiO_2	Al_2O_3	Cl	
630– 1	360	37.5	28.4	25.8	43.6	34.0	0.52	0.3	12.0	58.9	0.9
2		37.5	28.4	25.8	43.6	30.2	0.45	0.3	11.9	58.0	0.9
3		22.5	28.4	51.6	29.1	20.8	0.42	0.7	6.6	58.0	1.8
4		22.5	28.4	51.6	25.6	18.1	0.86	1.3	6.1	58.8	1.8
5		7.5	28.4	77.4	14.1	11.7	0.24	2.6	3.8	56.5	2.6
6		7.5	28.4	77.4	6.2	13.0	0.57	2.5	3.5	57.5	2.7
631–21	540	37.5	28.4	25.8	40.4	28.8	0.32	0.6	11.8	59.2	0.9
22		37.5	28.4	25.8	43.2	28.6	0.32	0.9	12.9	59.6	0.8
23		22.5	28.4	51.6	30.4	18.4	0.58	1.9	5.7	64.6	1.7
25		7.5	28.4	77.4	8.4	8.1	0.33	2.8	2.7	59.5	2.6
26		7.5	28.4	77.4	13.4	10.0	0.32	2.7	3.2	59.7	2.6

TABLE 39

COMPOSITION OF SOLID FORMED FROM MAGNESIUM SULPHATE, SODIUM SILICATE, AND SODIUM ALUMINATE AT 360 AND 540 DEG. F.

Test No.	Temperature deg. F.	Composition, per cent				Molar Ratios			
		CaO	SiO_2	Al_2O_3	H_2O	CaO	SiO_2	Al_2O_3	H_2O
630- 1.....	360	28.6	29.1	25.5	12.7	1	0.9	0.4	1.3
2.....		29.9	29.4	26.9	12.7	1	0.9	0.4	1.3
3.....		20.6	37.0	24.2	12.4	1	1.6	0.6	1.8
4.....		19.6	37.0	25.2	12.5	1	1.7	0.7	1.9
5.....		15.0	41.5	20.4	13.0	1	2.5	0.7	2.7
6.....		13.5	41.3	19.5	13.0	1	2.8	0.5	2.9
631-21.....	540	31.4	31.2	29.2	9.3	1	0.9	0.5	0.9
22.....		31.3	30.3	28.9	9.5	1	0.9	0.5	0.9
23.....		17.8	37.6	31.7	7.5	1	1.9	0.9	1.3
25.....		13.9	45.0	25.4	9.0	1	3.0	1.0	2.0
26.....		25.3	45.5	25.5	8.5	1	2.6	0.9	1.7

This would indicate that calcium alumino silicates are less soluble than magnesium alumino silicates.

The solids formed in these tests were analyzed as before, and the results are given in Table 39. The ratios correspond closely to those given in Table 38, and need no additional discussion. The solids formed throughout the tests were quite flocculent.

(g) *Conclusions.*—The summary of conclusions which may be drawn from the results of the study on the solubility of solid silicates is as follows:

(1) Analcite is more soluble at higher temperatures, and the solubility is greater with increased alkalinity, but the solubilities of silica and alumina are not in the same ratio as when combined in this complex silicate.

(2) In order to keep the silica content of the solution low, the magnesium to silica molar ratio in the solid must be greater than 1.

6. *Prevention of Sulphate Scale.*—One method of preventing the formation of calcium sulphate scale in steam boilers is to convert the calcium to a form which will not form scale. Under certain conditions the addition of sufficient sodium carbonate or sodium phosphate will prevent the formation of the sulphate scale.

Tests have been run using different sodium salts, in order to see if other chemicals could be used to prevent the sulphate scale. These tests have involved the use of sodium fluoride, cryolite, and sodium oxalate. The tests have been divided into the three following divisions:

(A) Solubility Tests Run in Bombs

(B) Solubility Tests at 212 deg. F.

(C) Scale Prevention Tests in Laboratory Boiler

TABLE 40

FLUORIDE, HYDROXIDE, AND CARBONATE CONTENT OF SOLUTIONS CONTAINING SODIUM FLUORIDE AND HYDROXIDE HEATED WITH SOLID CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added	
		F	OH	CO_3	CO_3/F	F	OH
		millimoles per liter				millimoles per liter	
579	360	11.5	6.25	1.6	0.14	12.5	6.5
		13.0	4.55	2.1	0.16	12.5	6.5
		17.0	4.40	4.2	0.25	25.0	6.5
		16.0	5.50	3.6	0.23	25.0	6.5
		31.8	4.07	6.6	0.21	37.5	6.5
		32.0	5.45	6.6	0.21	37.5	6.5
				Av.	0.20		
578	470	7.0	5.38	1.6	0.23	8.9	6.7
		5.6	4.80	2.3	0.41	8.9	6.7
		10.7	3.56	2.3	0.22	17.8	6.7
		14.3	3.88	5.0	0.35	26.7	6.7
		15.1	2.76	5.6	0.37	26.7	6.7
				Av.	0.32		
580	540	8.8	4.00	2.9	0.33	8.9	6.7
		10.7	5.00	3.0	0.28	8.9	6.7
		14.3	2.70	5.8	0.40	17.8	6.7
		21.2	4.73	7.4	0.35	26.7	6.7
		20.0	4.65	7.8	0.39	26.7	6.7
				Av.	0.35		

(A) Solubility Tests Run in Bombs

The same bombs were used for these tests as in those previously described. A list of the various tests run, and the numbers of the tables containing the results of these tests, is as follows:

Table No.	Solid Added	Solution Added
40	Calcium carbonate	Sodium fluoride, hydroxide
41	Calcium sulphate	Sodium fluoride, hydroxide
42	Calcium phosphate	Sodium fluoride, hydroxide
43	None	Cryolite and hydroxide
44	Calcium carbonate	Cryolite and hydroxide
45	Calcium sulphate	Cryolite and hydroxide
46	Calcium fluoride	Sodium carbonate, hydroxide
47	Calcium fluoride	Sodium phosphate, hydroxide
48	Calcium carbonate	Sodium oxalate, hydroxide
49	Calcium sulphate	Sodium oxalate, hydroxide
50	Calcium oxalate	Sodium carbonate, hydroxide

TABLE 41
FLUORIDE, SULPHATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM FLUORIDE AND HYDROXIDE HEATED WITH SOLID CALCIUM SULPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added		
		F	SO_4	OH	F/SO_4	F	OH	SO_4
		millimoles per liter						
589.....	360	0.5	5.6	1.9	0.10	8.9	6.6	...
		1.0	9.7	2.0	0.10	17.8	6.6	...
		1.0	9.5	2.4	0.11	17.8	6.6	...
		1.2	14.1	2.3	0.09	26.7	6.6	...
588.....	470	1.4	5.0	2.0	0.28	8.9	6.6	...
		1.8	3.7	1.0	0.48	8.9	6.6	...
		1.3	9.5	1.7	0.15	17.8	6.6	...
		1.4	9.3	1.5	0.16	17.8	6.6	...
		1.5	11.9	1.0	0.13	26.7	6.6	...
		1.6	13.4	1.3	0.12	26.7	6.6	...
546.....	470	1.4	8.7	10.5	0.16	17.8	16.6	3.2
		3.2	10.6	12.4	0.30	17.8	16.6	3.2
		3.0	13.7	10.7	0.22	17.8	16.6	6.5
		3.4	14.0	12.4	0.24	17.8	16.6	6.5
		3.3	20.8	11.3	0.16	17.8	16.6	13.0
		2.7	19.1	12.1	0.14	17.8	16.6	13.0
575.....	540	1.4	3.7	2.5	0.40	8.9	6.8	...
		1.6	3.8	3.1	0.43	8.9	6.8	...
		2.1	6.9	2.2	0.30	17.8	6.8	...
		3.1	9.5	2.3	0.32	26.7	6.8	...
		3.0	9.6	2.3	0.31	26.7	6.8	...

(a) *Fluoride Tests.*—Table 40 gives the results obtained when solutions containing sodium fluoride and sodium hydroxide were heated in contact with calcium carbonate in excess. The fluoride remained largely in solution. The ratio of the carbonate to the fluoride varied from 0.20 at 360 deg. F., to 0.35 at 540 deg. F. This would indicate that as long as the carbonate content is greater than 0.2 times the fluoride, the calcium carbonate would be formed in preference to the calcium fluoride as a solid. In the majority of boilers, the carbonate would be present in sufficient quantity to prevent the fluoride from forming unless excessive amounts of fluoride were present in solution.

In Table 41 are shown the results of tests run when the solid present at the beginning was calcium sulphate, and solutions containing sodium fluoride and sodium hydroxide were added. At 360 deg. F. the fluoride content dropped to about 1.3 millimoles (55 parts per million NaF), with the sulphate about 14 millimoles per liter (2000 parts per million Na_2SO_4), thus showing that the calcium fluoride would be formed in preference to the sulphate if over 55 parts

TABLE 42

PHOSPHATE AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM FLUORIDE AND HYDROXIDE HEATED WITH SOLID TRI-CALCIUM PHOSPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test		Added F
		PO_4	OH	
		millimoles per liter		
529.....	470	0.0	18.6	8.9
		0.0	20.2	8.9
		0.0	20.4	17.8
		0.0	22.3	26.7
		0.0	22.2	26.7

TABLE 43

FLUORIDE, ALUMINA, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING CRYOLITE AND SODIUM HYDROXIDE HEATED WITH NO SOLID PRESENT

Test No.	Temperature deg. F.	At End of Test			Added	
		F	Al_2O_3	OH	F	Al_2O_3
		millimoles per liter				
632.....	360	6.2	0.34	0.0	5.0	0.59
		6.7	0.28	0.1	5.0	0.59
		10.3	0.44	2.2	10.1	1.18
		12.5	0.55	2.4	10.1	1.18
		17.4	0.64	5.6	15.0	1.77
		16.7	1.30	5.4	15.0	1.77
633.....	405	5.4	0.78	0.7	5.0	0.59
		5.4	1.03	0.6	5.0	0.59
		9.4	0.78	0.7	10.1	1.18
		11.5	0.98	0.5	10.1	1.18
		15.6	0.83	3.4	15.0	1.77
		16.3	0.72	3.0	15.0	1.77
634.....	470	5.5	0.28	0.0	5.0	0.59
		10.6	0.48	1.8	10.6	1.18
		10.6	0.32	0.6	10.1	1.18
		16.5	0.46	1.2	15.0	1.18
		16.6	0.58	1.2	15.0	1.77
636.....	540	4.2	0.59	0.3	5.0	0.59
		10.8	0.55	0.9	10.1	1.18
		16.3	1.60	1.6	15.0	1.77
		15.1	0.63	1.6	15.0	1.77

per million of NaF were present, even with the sodium sulphate as high as 2000 parts per million. At 540 deg. F., apparently about 120 parts per million of NaF would be necessary to prevent calcium sulphate from forming, if the sodium sulphate were around 1400 parts per million.

TABLE 44

FLUORIDE, ALUMINA, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING CRYOLITE AND SODIUM HYDROXIDE HEATED WITH SOLID CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		F	Al_2O_3	OH	F	Al_2O_3
		millimoles per liter				
553.....	360	7.1	0.98	4.8	8.9	0.58
		6.4	0.91	4.3	8.9	0.58
		10.5	1.47	11.0	17.6	1.15
		10.5	1.50	10.9	17.6	1.15
		13.3	2.04	17.6	26.5	1.73
		16.0	1.98	17.8	26.5	1.73

TABLE 45

FLUORIDE, SULPHATE, ALUMINA, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING CRYOLITE AND SODIUM HYDROXIDE HEATED WITH SOLID CALCIUM SULPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test				Added	
		F	SO_4	Al_2O_3	OH	F	Al_2O_3
		millimoles per liter					
637.....	360	0.51	3.4	0.27	0.0	5.0	0.52
		0.51	3.3	0.32	0.0	5.0	0.52
		0.51	6.5	0.27	0.0	10.1	1.03
		0.70	6.1	0.43	0.0	10.1	1.03
		0.51	9.9	0.43	0.0	15.0	1.55
		0.80	9.3	0.40	0.0	15.0	1.55
554.....	360	0.69	3.9	0.34	2.1	8.9	0.58
		0.83	4.3	0.20	17.6	8.9	0.58
		0.29	7.5	0.83	7.1	17.8	1.16
		0.31	6.9	0.77	6.0	17.8	1.16
		0.19	10.3	1.35	10.4	26.7	1.74
		0.35	10.1	1.55	11.5	26.7	1.74
642.....	405	0.31	4.7	0.29	0.0	6.1	0.51
		0.31	4.6	0.36	0.0	6.1	0.51
		0.30	8.1	0.55	2.1	12.3	1.02
		0.31	8.5	0.55	2.6	12.3	1.02
		0.31	11.0	1.23	7.7	18.4	1.53
		0.20	12.2	1.19	4.9	18.4	1.53
643.....	470	0.65	3.7	0.33	0.3	6.1	0.51
		0.31	3.6	0.44	0.0	6.1	0.51
		0.30	6.4	0.75	5.1	12.3	1.02
		0.43	6.8	0.56	4.4	12.3	1.02
		0.16	9.7	1.82	8.6	18.4	1.53
		0.15	10.6	1.37	9.7	18.4	1.53
640.....	540	0.86	2.2	0.48	0.0	5.0	0.52
		0.88	2.5	1.04	0.0	5.0	0.52
		1.40	...	1.02	0.0	10.1	1.04
		1.20	8.0	0.70	1.0	15.0	1.56

TABLE 46

FLUORIDE, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM HYDROXIDE AND CARBONATE HEATED WITH SOLID CALCIUM FLUORIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			
		F	CO_3	OH	CO_3/F
		millimoles per liter			
587	360	3.6	1.0	3.8	0.27
		4.3	1.1	3.1	0.26
		4.6	2.1	3.5	0.46
		4.8	1.4	4.3	0.31
		5.9	1.7	3.8	0.30
		6.3	1.7	4.2	0.27
					Av. 0.32
586	470	2.8	1.5	3.4	0.52
		2.6	1.7	2.5	0.63
		5.4	2.3	2.7	0.43
		5.3	2.3	3.0	0.44
					Av. 0.50
585	540	3.7	1.5	2.8	0.41
		3.3	1.4	3.6	0.42
		4.0	1.8	3.1	0.46
		3.7	1.9	3.1	0.52
		4.8	1.9	5.4	0.40
		5.1	1.9	4.0	0.37
					Av. 0.43

When tri-calcium phosphate was heated in contact with solutions containing sodium fluoride and sodium hydroxide (Table 42), no phosphate was found in the solution at the end of the test. This showed that tri-calcium phosphate has a lower solubility than calcium fluoride, and the presence of a small amount of soluble phosphate in solution would cause the precipitation of the calcium phosphate in preference to the calcium fluoride.

In order to study the stability of cryolite solutions at the various temperatures encountered in boiler operation, alkaline solutions of cryolite were heated at temperatures between 360 and 540 deg. F. The results of these tests (Table 43) show that the fluoride remains in solution, while the alumina tends to be partially removed.

When solutions containing cryolite and sodium hydroxide were heated with calcium carbonate, there was not much change in the composition of the solution (Table 44), thus showing that the calcium carbonate was less soluble than the calcium fluoride.

When solutions containing cryolite, sodium hydroxide, and sodium sulphate were heated with an excess of calcium sulphate, the fluoride content of the resulting solutions was reduced to a low amount (Table 45). Thus, at temperatures between 360 and 470 deg. F. the fluoride

TABLE 47

FLUORIDE, PHOSPHATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING TRI-SODIUM PHOSPHATE AND SODIUM HYDROXIDE HEATED WITH SOLID CALCIUM FLUORIDE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		F	PO_4	OH	PO_4	OH
		millimoles per liter				
620	360	8.8	0.0	0.0	2.2	3.2
		8.8	0.0	0.0	2.2	3.2
		15.0	0.0	0.5	4.5	3.2
		12.5	0.0	0.5	4.5	3.2
		23.5	0.0	0.9	6.7	3.2
		23.0	0.0	0.8	6.7	3.2
621	405	8.3	0.0	0.2	2.4	3.4
		8.5	0.0	0.0	2.4	3.4
		15.7	0.0	0.5	4.8	3.4
		14.7	0.0	0.6	4.8	3.4
		23.2	0.0	1.1	7.2	3.4
		23.2	0.0	1.3	7.2	3.4
622	470	8.3	0.0	0.1	2.4	3.4
		8.3	0.0	0.2	2.4	3.4
		13.1	0.0	0.8	4.8	3.4
		14.3	0.0	0.5	4.8	3.4
		21.0	0.0	0.6	7.2	3.4
		20.4	0.0	1.2	7.2	3.4
623	540	8.0	0.0	0.0	2.6	3.5
		8.1	0.0	0.0	2.6	3.5
		13.8	0.0	0.0	5.2	3.5
		13.5	0.0	0.3	5.2	3.5
		23.8	0.0	0.0	7.8	3.5
		23.6	0.0	0.9	7.8	3.5

was reduced to around 0.40 millimole (16 parts per million NaF) when alumina was present from the cryolite. When alumina was absent, as in the tests when sodium fluoride was added (Table 41), about 55 parts per million of sodium fluoride was necessary to prevent the sulphate from remaining stable. This indicates that the presence of aluminate aids in the removal of calcium sulphate from the solid phase.

In order to check further the tests run to study the relation between the solubility of calcium carbonate and calcium fluoride, solid calcium fluoride was heated in contact with solutions containing sodium hydroxide and carbonate. The results of these tests, reported in Table 46, show that the carbonate is reduced to a definite amount, depending on the fluoride content. The ratio of carbonate to fluoride at the various temperatures agrees very well with similar data collected when the equilibrium was approached from the other direction (Table 40).

The addition of alkaline tri-sodium phosphate solutions to calcium

TABLE 48

OXALATE, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM OXALATE AND HYDROXIDE HEATED WITH SOLID CALCIUM CARBONATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		Oxalate	CO_3	OH	Oxalate	OH
		millimoles per liter				
605	405	9.4	1.8	0.6	11.9	2.0
		9.3	2.2	1.7	11.9	2.0
		10.5	2.8	2.2	11.9	5.0
		10.9	1.8	3.2	11.9	5.0
		11.4	1.7	7.8	11.9	10.0
		10.9	...	8.0	11.9	10.0
606	470	0.2	7.3	0.0	12.0	2.0
		0.3	12.5	0.0	12.0	5.0
		0.2	14.3	0.0	12.0	5.0
		1.5	11.0	0.0	12.0	10.0
		0.5	17.1	0.0	12.0	10.0
607	540*	0.3	17.1	0.0	12.0	2.0
		0.2	15.8	0.0	12.0	2.0
		0.2	15.6	0.0	12.0	5.0
		0.2	19.3	0.0	12.0	5.0
		0.1	14.1	0.0	12.0	10.0
		0.1	14.8	0.0	12.0	10.0

*No solid added.

fluoride caused the formation of sodium fluoride, and reduced the phosphate content to a very low amount (Table 47). This checked the data reported in Table 42.

The data collected from these solubility tests on fluorides may be summarized as follows:

(1) Calcium fluoride is less soluble than calcium sulphate, and more soluble than calcium carbonate or phosphate, at the temperatures studied.

(2) The presence of over 50 parts per million of sodium fluoride in solution should prevent the formation of calcium sulphate at temperatures up to 470 deg. F., even when the sodium sulphate content is around 2000 parts per million.

(3) The presence of aluminate in solution aids in the precipitation of the calcium fluoride.

(b) *Oxalate Tests.*—When solutions containing sodium oxalate and sodium hydroxide were heated in contact with calcium carbonate up to 405 deg. F., the oxalate remained in solution in amounts equal to those added (Table 48). This indicated that the calcium carbonate was less soluble than the calcium oxalate. At 470 and 540 deg. F. the oxalate content was reduced to a low amount, and the carbonate con-

TABLE 49

OXALATE, SULPHATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM OXALATE AND HYDROXIDE HEATED WITH SOLID CALCIUM SULPHATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		Oxalate	SO_4	OH	Oxalate	OH
		millimoles per liter				
596-A	360	0.33	6.9	0.0	6.0	1.6
		0.52	12.5	0.0	12.0	1.6
		0.38	12.6	0.0	12.0	1.6
		1.15	17.2	0.0	18.0	1.6
603	360	0.65	12.5	1.5	12.0	6.1
		0.81	12.2	2.0	12.0	6.1
		0.54	13.1	7.0	12.0	12.2
		0.41	13.0	7.4	12.0	12.2
		0.61	13.6	12.2	12.0	18.3
		1.31	11.4	13.6	12.0	18.3
597	405	0.46	6.8	0.0	6.0	1.6
		0.46	6.7	0.0	6.0	1.6
		0.80	11.8	0.0	12.0	1.6
		1.27	14.4	0.0	12.0	1.6
		0.99	17.7	0.0	18.0	1.6
		1.09	16.8	0.0	18.0	1.6
598	470	0.34	4.0	0.0	6.0	2.1
		0.30	2.8	0.0	6.0	2.1
		0.30	7.2	0.0	12.0	2.1
		0.25	6.8	0.0	12.0	2.1
		0.33	8.7	0.0	18.0	2.1
		0.28	10.6	0.0	18.0	2.1
611	540	0.18	11.7	0.0	12.0	5.8
		0.18	14.1	0.0	12.0	11.6
		0.25	16.7	0.0	12.0	11.6
		0.16	15.6	0.0	12.0	17.4
		0.14	17.5	0.0	12.0	17.4

tent increased. The reduction of the hydrate content to zero at these temperatures indicated that the oxalate decomposed.

Tables 49 and 50 contain the results of tests run to determine the relative solubility of calcium sulphate and calcium oxalate. At temperatures up to 405 deg. F. the oxalate precipitated in preference to the sulphate; however, at 470 deg. F. the oxalate decomposed.

When calcium oxalate was heated in contact with solutions containing sodium hydroxide and sodium carbonate, the carbonate content was reduced and the soluble oxalate was formed. However, the carbonate was not reduced to below 3.5 millimoles—about 350 parts per million Na_2CO_3. This indicated that calcium carbonate would be formed in preference to calcium oxalate, if the sodium carbonate content were below 350 parts per million, and the temperature below 470 deg. F.

The results of oxalate tests were not very promising, and show that

TABLE 50

OXALATE, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM CARBONATE AND HYDROXIDE HEATED WITH SOLID CALCIUM OXALATE IN EXCESS

Test No.	Temperature deg. F.	At End of Test			Added	
		Oxalate	CO_3	OH	CO_3	OH
		millimoles per liter				
616	360	1.7	3.8	0.6	3.0	2.5
		1.9	3.9	0.6	3.0	2.5
		3.7	3.6	0.5	6.0	2.5
		6.0	3.5	0.5	9.0	2.5
		6.1	4.0	0.4	9.0	2.5
617	405	1.7	4.0	0.2	3.4	2.2
		1.9	4.1	0.3	3.4	2.2
		3.5	3.6	0.5	6.8	2.2
		3.8	4.6	0.4	6.8	2.2
		5.6	4.0	0.5	10.2	2.2
		5.6	4.5	0.4	10.2	2.2
618	470	0.2	2.3	0.0	3.4	2.2
		0.2	2.6	0.0	3.4	2.2
		0.2	4.6	0.0	6.8	2.2
		0.2	4.7	0.0	6.8	2.2
		0.2	4.0	0.0	12.2	2.2
		0.2	5.7	0.0	12.2	2.2
619	540	0.2	5.7	0.0	3.2	1.8
		0.2	7.4	0.0	6.4	1.8
		0.4	6.2	0.0	6.4	1.8
		0.2	12.1	0.0	9.6	1.8
		0.1	14.2	0.0	9.6	1.8

TABLE 51

SOLUBILITY OF SYNTHETIC CRYOLITE

In Dilute Sodium Hydroxide Solution at 70 deg. F.

NaOH Present in grams per liter	Cryolite grams per liter	NaOH Present in grams per liter	Cryolite grams per liter
0	0.082	2.68	3.62
1.34	2.15	5.38	7.76

TABLE 52

ANALYSIS OF UNIVERSITY OF ILLINOIS WATER

Ions	Parts Per Million	Ions	Parts Per Million
SiO_2	14.0	Na	34.8
Ca	66.9	K	4.1
Mg	31.4	SO_4	1.2
NH_4	5.3	Cl	4.0

TABLE 53
EFFECT OF SODIUM FLUORIDE ON UNIVERSITY OF ILLINOIS WATER AT 212 DEG. F.

Sample No.	Treatment	NaF Added p.p.m.	Solution at End p.p.m.			
			SiO_2	Al_2O_3	Ca	Mg
9A-11	None	0	18.0	11.3	62.5	31.4
9A-12	Boil 4 min., filter immediately	0	20.6	8.7	37.6	32.3
9A-13	Boil 4 min., filter immediately	25	16.2	12.2	45.2	31.5
9A-14	Boil 4 min., filter immediately	50	20.0	14.5	66.6	28.6
9A-15	Boil 4 min., filter immediately	100	17.4	19.4	68.9	31.5
9A-16	Boil 4 min., filter immediately	200	18.0	14.2	60.2	34.0
10-1	None	0	23.2	8.9	67.5	30.3
10-2	Boil 4 min., filter 18 hr. later	0	....	9.2	43.4	29.2
10-3	Boil 4 min., filter 18 hr. later	25	18.0	10.2	47.4	28.0
10-4	Boil 4 min., filter 18 hr. later	50	21.2	9.0	68.3	32.6
10-5	Boil 4 min., filter 18 hr. later	100	32.8	13.0	12.8	25.6

TABLE 54
EFFECT OF CRYOLITE ON UNIVERSITY OF ILLINOIS WATER AT 212 DEG. F.

Sample No.	Treatment	Cryolite Added p.p.m.	Solution at End p.p.m.			
			SiO_2	Al_2O_3	Ca	Mg
11A-11	None	0	25.2	11.0	64.3	31.8
11A-12	Boil 4 min., filter immediately	0	26.4	13.3	27.2	29.1
11A-13	Boil 4 min., filter immediately	25	33.6	15.9	42.9	34.9
11A-14	Boil 4 min., filter immediately	50	31.9	14.8	46.7	38.1
11A-15	Boil 4 min., filter immediately	100	26.1	28.7	63.1	28.4
11 -6	Boil 4 min., filter immediately	200	9.3	54.2	60.7	....
12A-11	None	0	21.2	8.1	63.2	30.1
12A-12	Boil 4 min., filter 18 hr. later	0	24.4	8.1	35.9	31.9
12A-13	Boil 4 min., filter 18 hr. later	25	26.1	13.0	42.8	24.2
12A-14	Boil 4 min., filter 18 hr. later	50	34.5	11.0	50.3	19.4
12A-15	Boil 4 min., filter 18 hr. later	100	33.6	15.3	43.6	24.1
12A-16	Boil 4 min., filter 18 hr. later	200	12.5	10.5	59.3	32.8

the use of sodium oxalate has very little, if any, advantage over that of salts now being used to prevent sulphate scale.

(B) Solubility Tests at 212 deg. F.

In order to study further the treatment of boiler water with fluorides, solutions of University of Illinois water were boiled in contact with various concentrations of fluoride solutions (sodium and cryolite). First, the solubility of cryolite at 70 deg. F. in distilled water, to which various amounts of sodium hydroxide had been added, was studied. Table 51 shows the results obtained. The solubility of the cryolite increases as the hydroxide content increases.

An analysis of University of Illinois water is given in Table 52.

TABLE 55

EFFECT OF SODIUM FLUORIDE ON CALCIUM SULPHATE AND MAGNESIUM SULPHATE SOLUTIONS AT 212 DEG. F.

Sample No.	Treatment	NaF Added p.p.m.	Solution at End p.p.m.		
			Ca	SO_4	Mg
5-23	None	0	34.1	81.6	....
6- 1	Boil 4 min., filter immediately	75	12.0	70.3	....
6- 2	Boil 4 min., filter immediately	150	3.2	70.1	....
6- 3	Boil 4 min., filter immediately	300	2.8	74.5	....
6- 4	Boil 4 min., filter immediately	600	2.8	75.2	....
7- 1	None	0	....	768	211
8- 1	Boil 4 min., filter immediately	75	....	772	188
8- 2	Boil 4 min., filter immediately	150	....	785	197
8- 3	Boil 4 min., filter immediately	300	....	803	153
8- 4	Boil 4 min., filter immediately	600	....	778	80

TABLE 56

EFFECT OF CRYOLITE ON CALCIUM SULPHATE AND MAGNESIUM SULPHATE SOLUTIONS AT 212 DEG. F.

Sample No.	Treatment	Cryolite Added p.p.m.	Solution at End p. p. m.		
			Ca	SO_4	Mg
5-23	None	0	34.1	81.6	...
5-24	Boil 4 min., filter immediately	60	28.5	82.1	...
5-25	Boil 4 min., filter immediately	60	25.2	63.8	...
5-26	Boil 4 min., filter immediately	120	24.8	62.4	...
5-27	Boil 4 min., filter immediately	240	12.9	57.3	...
7- 1	None	0	....	768	211
7- 2	Boil 4 min., filter immediately	0	....	766	203
7- 3	Boil 4 min., filter immediately	60	....	781	193
7- 4	Boil 4 min., filter immediately	120	....	781	193
7- 5	Boil 4 min., filter immediately	240	....	767	185
7- 6	Boil 4 min., filter immediately	480	....	772	162

This water contains bicarbonate hardness, no sulphate, and sodium bicarbonate, so that, on boiling, sodium carbonate forms, and the calcium tends to be precipitated. The solutions to be tested were boiled 4 minutes, and then either filtered at once or let stand 18 hours and then filtered. Various amounts of sodium fluoride or cryolite were added to the solutions prior to boiling. Table 53 gives the results of the tests run when sodium fluoride was added. When the solution was boiled in the absence of the fluoride, the calcium was reduced from 67 to around 40 parts per million. When 25 parts per million of sodium fluoride were added, the calcium was only reduced to 45 parts per million, and when 50 parts per million were added, the calcium

was not reduced at all. This effect was noticed in both sets of tests, in those in which the solution was filtered hot, as well as in those in which the solution was filtered after standing 18 hours.

When cryolite was used instead of sodium fluoride, the calcium was also held in solution. However, the cryolite did not appear to be as effective as the sodium fluoride (Table 54).

Solutions of calcium sulphate and magnesium sulphate in distilled water were treated with sodium fluoride and cryolite, boiled 4 minutes, and filtered immediately. The results, given in Table 55, showed that the magnesium was not affected by the sodium fluoride until over 300 parts per million were present. The calcium content was reduced to a very low figure, 3.0 parts per million. When cryolite was added, the calcium content was only reduced from 34 to 25 parts per million, even when 120 parts per million of cryolite were present (Table 56). The cryolite had no appreciable effect on the magnesium present. These results indicate that cryolite will tend to retard the reaction between the fluoride and calcium sulphate, and the addition of cryolite to a feed water would not cause any precipitation of the calcium until the water reached the boiler.

(C) Scale Prevention Tests in Laboratory Boiler

In order to study the effectiveness of the fluorides and oxalates in the prevention of scale, tests were run in the laboratory scaling boiler. The boiler and the method of operation are described in Bulletin 261.* The tests run and the results obtained are given in Table 57.

The tests run at 150 pounds steam pressure showed that when the fluorine content was above 30 parts per million, no appreciable scale formed on the heating surface. At 250 pounds steam pressure 32 parts per million of fluorine prevented a scale from forming. When the steam pressure was increased to 500 pounds per square inch, 40 parts per million of fluorine appeared to be the amount necessary to prevent scale from forming.

Cryolite proved as effective as sodium fluoride, and had the added advantage of reducing the caustic alkalinity of the boiler water.

The conclusions which may be reached from the data collected are as follows:

(1) Sodium fluoride, when used in boilers at pressures up to 500 pounds per square inch, will prevent calcium sulphate scale when the flourine content is above 40 parts per million.

(2) Cryolite, when used in boilers at pressures up to 500 pounds

*"The Cause and Prevention of Calcium Sulphate Scale in Steam Boilers," Univ. of Ill. Eng. Exp. Sta. Bul. 261, 1933.

TABLE 57
TESTS RUN IN SCALING BOILER

Test No.	Steam Pressure lb. per sq. in., gage	Concentration in Boiler Water parts per million								Time of Test days	Solid Added to Boiler	Results
		Na_2SO_4	NaOH	Na_2CO_3	NaCl	F	Oxalate	SiO_2	Al_2O_3			
41	150	1200	180	12	60	38	...	...	...	10	CaF_2	No scale
49	150	1000	200	20	60	43	...	...	...	10	CaF_2, $CaCO_3$	No scale
51*	150	1000	120	15	60	30	...	...	20	12	CaF_2, $CaCO_3$	No scale
42	150	1000	180	20	60	53	...	100	...	8	CaF_2, $CaCO_3$	Trace of scale
43	150	1000	240	20	60	40	...	5	...	8	{MgO, $CaCO_3$} CaF_2	Light scale
54	150	1000	200	17	60	..	100	...	...	10	$CaCO_3$	No scale
50	250	1000	200	15	60	32	...	...	...	10	$CaCO_3$, CaF_2	No scale
39	500	900	50	10	60	23	...	...	...	8	CaF_2	Light scale
38	500	850	120	10	60	68	...	...	...	7	CaF_2	No scale
55	500	1000	80	14	60	55	...	...	...	18	CaF_2	No scale
57*	500	1000	10	15	60	40	...	...	...	14	CaF_2	Light scale
58*	500	1000	50	10	60	80	...	...	...	11	CaF_2	No scale
40	500	1000	160	10	60	30	...	...	...	11	$CaCO_3$, CaF_2	Light scale
45	500	1000	200	15	60	20	...	...	...	9	$CaCO_3$, CaF_2	Light scale
44†	500	1000	280	12	60	30	...	...	40	9	$CaCO_3$, CaF_2	Light scale
48	500	1000	280	15	60	44	...	...	...	12	$CaCO_3$, CaF_2	No scale
47	500	1000	240	15	60	0	...	...	...	12	$CaCO_3$	Heavy scale
46	500	1000	160	20	60	38	...	...	...	18	$CaCO_3$	Light scale
52‡	500	1000	200	15	60	0	2	...	...	11	MgO	No scale

*Cryolite used in place of NaF, as in other tests.
†Sodium aluminate added to solution fed to boiler.
‡Silicate solution added 500 p.p.m., SiO_2 reduced to 2 p.p.m. by excess MgO in boiler.

per square inch, will prevent calcium sulphate scale when the flourine content is above 40 parts per million.

(a) *Comparison of Effectiveness of Fluoride and Metaphosphate for Scale Prevention.*—Sodium metaphosphate is being used for boiler feed water treatment to prevent sulphate scale. It has been stated that if the metaphosphate is present in excess it will not cause precipitation in the feed lines, but when it enters the boiler it will precipitate the calcium as the insoluble phosphate and reduce the caustic alkalinity of the boiler water.

Cryolite will also retard the precipitation of the calcium in the feed lines, prevent sulphate scale in the boiler, and reduce the caustic alkalinity of the boiler water.

A comparison of the alkalinity-reducing power of sodium metaphosphate and cryolite is given in Table 58. This shows that practically the same amount of cryolite is required per pound of calcium treated as of the metaphosphate. However, the alkalinity-reducing power of the cryolite is 1.4 times greater than that of the metaphosphate per pound of salt used.

These properties of cryolite would indicate that there is a possible field for its utilization in boiler feed water treatment.

III. Organic Studies

7. *Object of Organic Studies.*—Organic matter has been used in the treatment of boiler water to prevent scale formation for many years. There are available many commercial organic materials or compounds which are effective under certain conditions in the removal and prevention of boiler scale. Many operating engineers as well as chemical engineers have hesitated to use these organic materials since they could not clearly comprehend the manner in which they functioned, and because of this they feared that they could not control the action of these organic materials as definitely as they could that of the inorganic chemicals used in boiler water treatment. However, in recent years experience with these organic methods of boiler water treatment has definitely shown that there is a specific field for their utilization, and that further definite information relative to their action would advance their use to a great extent. Furthermore, a thorough knowledge of the action of these organic materials which could be brought about by a study of the composition of the effective ingredients might result in the production of a synthetic organic product which would have all the advantages and none of the dis-

TABLE 58

COMPARISON OF ACTION OF SODIUM METAPHOSPHATE AND CRYOLITE WHEN USED TO TREAT CALCIUM SULPHATE AND CALCIUM CARBONATE SOLUTIONS

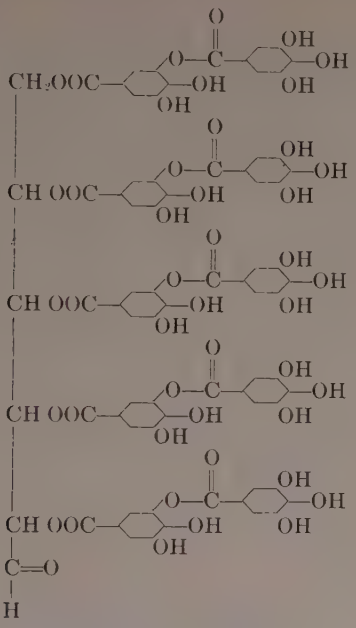
Calcium Salt Present	Amount of Salt Necessary to React with One Pound Calcium		Sodium Hydroxide Neutralized per Pound Calcium	Sodium Hydroxide Formed per Pound Calcium	Total Sodium Hydroxide Formed per Pound Calcium
	$NaPO_3$	Cryolite			
$CaSO_4$	1.7	....	1.32	....	−1.32
$CaSO_4$	...	1.76	2.0	....	−2.00
$CaCO_3$	1.7	....	....	0.32	0.32
$CaCO_3$	...	1.76	....	2.00	2.00

When no calcium is present, 1 lb. $NaPO_3$ neutralizes 0.39 lb. NaOH.
When no calcium is present, 1 lb. cryolite neutralizes 0.57 lb. NaOH.

advantages of the present materials. Thus it is highly probable that an organic chemical could be produced which would be effective in preventing scale at much higher steam pressures than those now in use. With a definite compound available, and a clear explanation of its action, the present resistance of the power plant executives to the utilization of organic compounds would be entirely overcome. It was with these ideas in mind that this research was started.

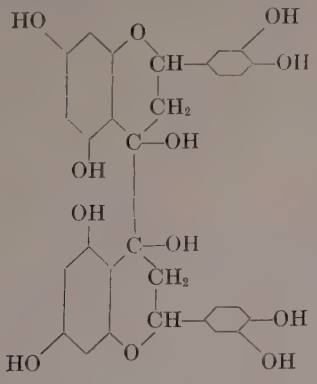
8. *Composition of Organic Materials Used in Industrial Work.*— Various types of organic materials have been used in boiler water treatment. The so-called tannin extracts appear to predominate; other plant extracts such as starches, gels, etc. are also used to a large extent. To make a thorough study of all the compounds now in use would be prohibitive. Consequently, the present research has been confined to the plant extracts commonly referred to as tannins. A small amount of work has been started on the starches and other materials.

Tannin extracts obtained from different sources show very different properties which are apparently due to the foreign matter extracted with the tannin, as well as to the fact that different types of tannins are extracted. The tannins may be roughly classified under two headings, namely, gallotannin and phlobatannin, the structure of the gallotannin being as follows:



Pentagallogalloylglucose

The structure of a typical phlobatannin is as follows:

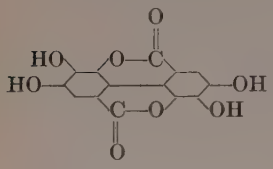


bis-(5:7:3′:4′-tetrahydroxy) flavpinacol

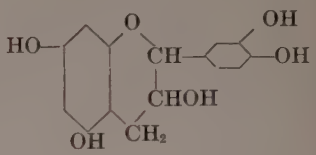
With such a difference in structure these two tannins might be expected to behave differently, and experience justifies this expectation.

There are also present various amounts of catechin, ellagic acid and other compounds. The structures of these compounds are as follows:

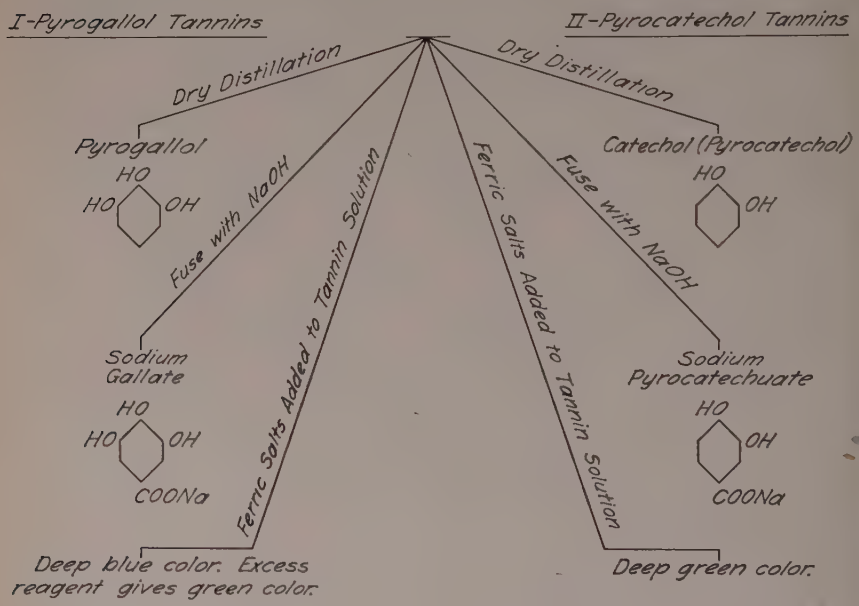
Ellagic acid formula



Catechin formula



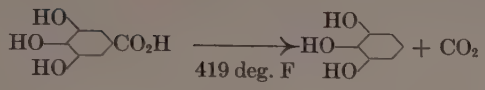
An older system of classification of tannins is as follows:



All tannins are precipitated by lead acetate, but if the solution is first made approximately normal to acetic acid, the pyrogallol tannins only are precipitated by the addition of lead acetate, the catechol tannins remaining in solution. On the other hand, the catechol tannins are precipitated by the addition of an excess of bromine water, while the pyrogallol tannins remain in solution.

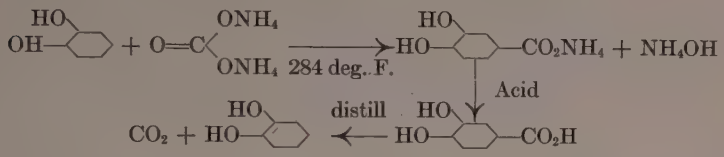
Tannin Derivatives

Gallic acid:



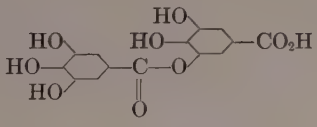
It crystallizes with one molecule of water. This is given off at 212-248 deg. F. It does not have a definite melting point.

Pyrocatechuic acid:



Ferric chloride imparts to an aqueous solution of pyrocatechuic acid a bluish green color. The blue changes to red on the addition of alkalies.

Digallic acid:



It was Schiff's idea that tannin and digallic acid are the same. This was later disproved.

The gelatin-salt test for tannin:

To the tannin solution add one drop of salt-gelatin solution; a precipitate or turbidity indicates the presence of tannin.

The optimum pH value for this test is 3.5 to 4.5.

The gelatin-salt solution is prepared by adding 10 grams of gelatin to 100 grams of salt and diluting with water to a volume of one liter.

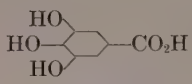
All tannins are active reducing agents. They reduce Fehling's solution and absorb oxygen from the air, the reaction taking place rapidly in an alkaline solution, forming colored oxidation products.

Gallic Acid

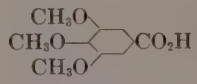
On hydrolysis tannins and related substances give gallic acid as the chief product. A small amount of glucose or other sugars, depending on the source of the tannin, is also produced by hydrolysis of tannin. This fact was definitely established by Emil Fischer. Since tannic acid is known to be a desirable constituent of materials used for the prevention or reduction of boiler scale, it is proposed to study the effect of gallic acid (which is derived from tannin) and its derivatives.

Gallic Acid and Some Derivatives

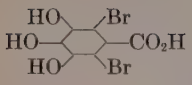
The formulas for gallic acid and some of its derivatives are as follows:



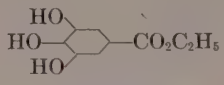
Gallic Acid



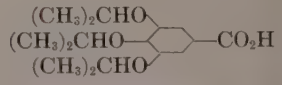
Trimethylgallic Acid



Dibromogallic Acid



Ethylgallate



Tri-isopropylgallic Acid

9. *Laboratory Tests of Various Organic Materials.*—

(A) Tests on Calcium Sulphate and Calcium Carbonate at 212 deg. F.

(1) Scale Tests

In order to obtain a measure of the effectiveness of the organic materials in preventing scale at 212 deg. F., tests were run in the apparatus shown in Figure 11. The solutions to be tested were fed at a constant rate into the flask. The steam pressure was 5 lb. per sq. in. and the steam in going through the steel pipe heated the solution to boiling. A constant level was maintained by means of the overflow, and the solution did not concentrate from evaporation due to the action of the reflux condenser. Two types of solutions were used, one saturated with calcium sulphate at room temperature, and the other saturated with calcium carbonate at room temperature. The duration of the tests was about 4 hours.

The first tests were run using the saturated calcium sulphate solution. At the end of four hours the tube was covered with a heavy white crystalline scale, as shown in Fig. 12. This scale had formed slowly but consistently during the entire test. When 30 p.p.m. of cutch (No. 1) was added to the solution of calcium sulphate prior to feed-

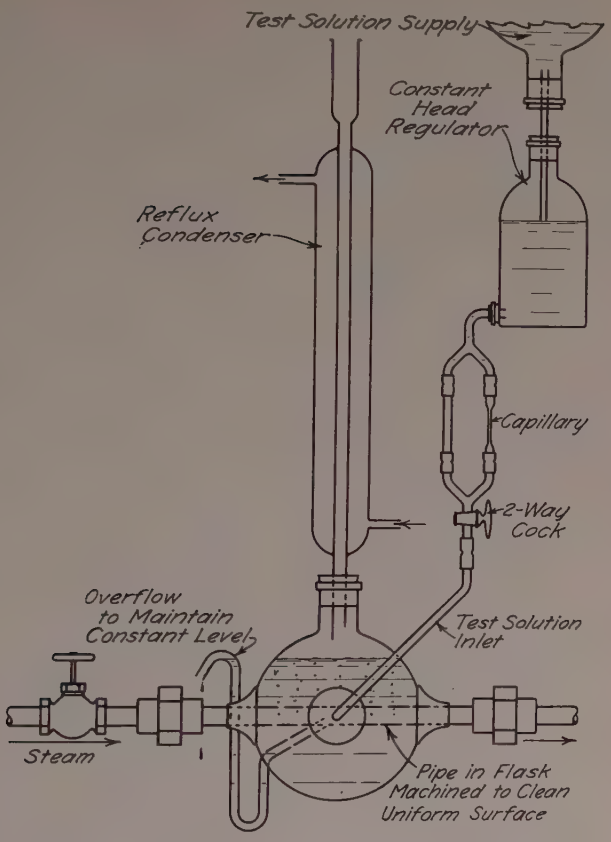
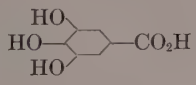


FIG. 11. APPARATUS USED FOR SCALE PREVENTION TESTS

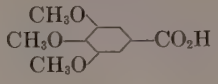
ing to the flask, the solution darkened in the boiling flask and a very small amount of scale formed. Since gallic acid



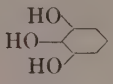
is one of the possible compounds formed by the decomposition of tannin, it was thought advisable to run a test with this pure organic compound. Again 30 p.p.m. were used, and at the end of the test the tube was darkened and covered with a thick black deposit, but no appreciable scale was formed. Since this solution might be acid and cause some attack on the tube, the prevention of calcium sulphate scale might be attributed to this action. In order to see if this were

the case, fine crystals of calcite ($CaCO_3$) were added to the boiling solution in the flask. The calcite kept the pH value of the solution above 8 at all times, and thus prevented any acid attack on the tube. However, the scale did not form, and the tube was still blackened.

In order to determine whether this scale prevention property was due to the OH or the CO_2H attached to the benzene ring, trimethylgallic acid



was tested. The tests resulted in a heavy scale forming on the tube, and demonstrated that it was apparently the hydroxyl ion distribution on the ring which was helping to prevent scale. If this were the case, and the acid radical were eliminated, the compound would be pyrogallol

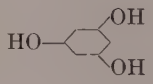


which should be effective in preventing scale. Tests run using pyrogallol gave a scale-free tube without the blackening (Fig. 13). In order to decide whether the prevention of scale was due to the anti-oxidant property of pyrogallol, or merely to the presence of the hydroxy groups in the benzene nucleus a series of two types of compounds was tried:

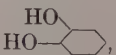
(a) substituted hydroxy benzene derivatives having various structural configurations;

(b) organic compounds having anti-oxidant properties but containing no hydroxy groups.

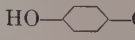
The first substituted hydroxy benzene derivatives tested constituted the trihydroxy type with the hydroxy group in various positions on the benzene nucleus. Phloroglucinol



gave a medium scale. The dihydroxy compounds tested were catechol



hydroquinone



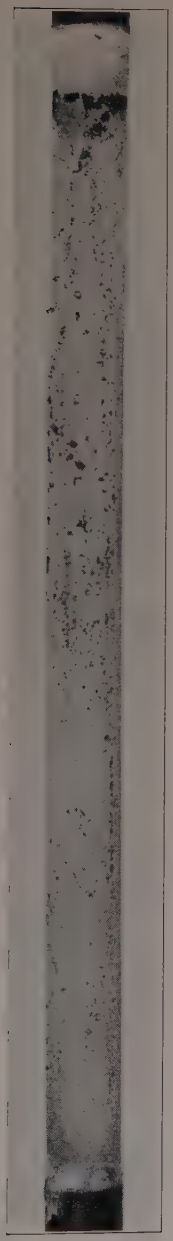


FIG. 12. CALCIUM SULPHATE SCALE FORMED AT 212 DEG. F.

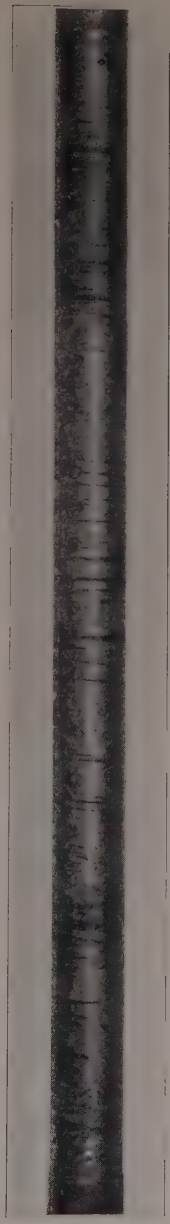
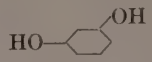
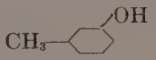


FIG. 13. SCALING TUBE SHOWING EFFECT OF INHIBITOR AT 212 DEG. F.

(both giving very slight scale), and resorcinol



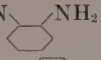
(giving a medium to heavy scale). The monohydroxy derivative tested was metacresol



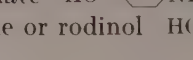
and a heavy scale resulted.

These results indicated that in the dihydroxy benzene derivatives more beneficial results are obtained when the OH groups are ortho or para to each other than when they are situated meta to each other.

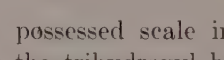
Anti-oxidants were then tried in order to see if this property was necessary to have scale prevention. The following anti-oxidants were tested:

o—phenylenediamine 

p—phenylenediamine

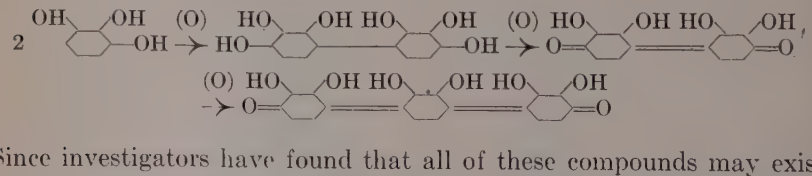
p—methylaminophenolsulphate 

p—aminophenohydrochloride or rodinol

amidol 

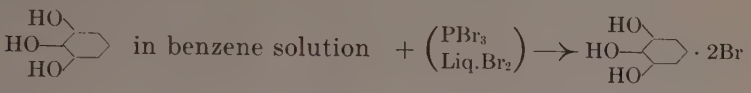
None of these possessed scale inhibiting properties, which indicated clearly that the trihydroxyl benzene derivatives were best for scale prevention. These types of compounds are readily oxidized, and it was thought that the oxidation products might be preventing the scale.

Pyrogallol, when oxidized in alkaline solution, might act as follows:



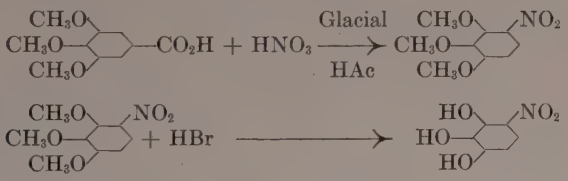
Since investigators have found that all of these compounds may exist in an alkaline solution of pyrogallol, a method of preventing this oxidation and linkage would indicate whether the beneficial results were due to pyrogallol itself, to its oxidation products, or to a mixture of the two.

Dibromopyrogallol (the exact location of the Br is not known) has been synthesized.



This compound, when dissolved in water, becomes a beautiful clear pink, changing through yellow brown to dark brown, and then to black, indicating that some sort of oxidation is probably taking place. In the testing unit the dibromopyrogallol prevented the formation of all but a *very* slight deposit of scale from a saturated calcium sulphate solution. Since the compound in solution did undergo the color change mentioned, there was no conclusive proof that either the pyrogallol or the linked product is solely responsible for the scale-inhibiting properties.

The preparation of nitropyrogallol was attempted by passing nitrous acid through an ether solution of pyrogallol. This method did not give the desired product, so the nitration of trimethylgallic acid in glacial acetic acid solution was tried.



Methyl groups are split off by refluxing with HBr

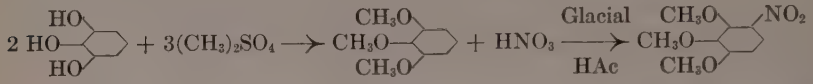
The difficulties encountered in this preparation were numerous, a few of them being given in the following.

A trial at 32 deg. F. resulted in no nitration at all, while at fairly high temperatures the di-nitro compound was formed. Some measure of success was obtained by using a nitration temperature of from 77 to 86 deg. F.

The trimethoxymononitro compound was not difficult to obtain pure enough to check the literature melting point of 212 deg. F. The final product obtained in each case did not check the literature melting point of 323 deg. F. given for nitropyrogallol, and all attempts to prepare a compound which would check this figure were fruitless. After several attempts, a product melting over a range from 356 to 370 deg. F. was prepared. None of the melting points given in Richter for the possible compounds gave even an indication as to what had been synthesized. This, together with the fact that the literature

references were quite old, encouraged the assumption that the product was mononitropyrogallol.

Trimethylpyrogallol was prepared according to the following equation:



The nitrating and splitting of this ether has not as yet been carried out.

In the testing unit the 356-370 deg. F. material (50 p.p.m.) gave a light to medium scale. When run in an alkaline solution, almost no scale at all was formed, but a very distinct color change from yellow to a deep persistent red took place upon addition of the alkali. This red color remained unchanged after five days exposure to the air. The brownish-black color observed in alkaline solutions of pyrogallol changed to clear yellow after several hours. The red color changed back to yellow at once upon addition of acid in excess of alkali present. Hydrogen peroxide oxidized the compound in alkaline solution to a clear yellow in about 4 hours.

Another mode of attacking this problem would be the preparation, isolation, and trial of one or more of the oxidation products of pyrogallol. Oxidation of pyrogallol in barium hydroxide solution should yield hexahydroxydiphenyl

but after numerous attempts and modifications of procedure no product was obtained. Oxidation of pyrogallol in potassium hydroxide solution and extraction of the oxidized product with ether should give 2:3:2′:3′:2″:3″-hexahydroxytriphenoquinone. This method was also unsuccessful, since on each occasion the first ether extraction failed to give any of the desired product.

Pyrogallol

Pyrogallol itself was found to be quite effective in scale prevention at concentrations as low as 5 p.p.m., 10 p.p.m. giving better results, however. Various tests have been run to determine the tendency of pyrogallol to oxidize in alkaline solutions. Tests using boiled distilled water with pyrogallol at 100 parts per million were found to give a negative test for pyrogallol after 45 minutes. This indicates that the pyrogallol is rapidly oxidized in alkaline solution and probably does

not exist very long in the testing unit as pyrogallol itself, but as its oxidation products.

A compound of iron and gallic acid was prepared by mixing gallic acid and ferrous sulphate together dry and adding sodium hydroxide. Iron-pyrogallol compound was prepared in a similar manner.

Flasks were prepared containing equivalent concentrations of iron-gallic acid compound, iron-pyrogallol compound, pyrogallol and iron filings, and pyrogallol alone. One set of these flasks was oxidized by bubbling CO_2-free air through them for 16 hours. Another set was oxidized by adding hydrogen peroxide. The set oxidized by air showed excellent scale-inhibiting properties when run in the testing unit. Of the ones oxidized with hydrogen peroxide, the pyrogallol and gallic acid compounds of iron showed heavy scaling in the unit, while the pyrogallol plus iron filings and the pyrogallol alone showed only slight scaling on the tube. These results strengthen the assumption that the oxidized products of pyrogallol are responsible for the scale-inhibiting properties. The strenuous oxidation with hydrogen peroxide renders pyrogallol ineffective if continued too long, however.

Starch

The hydrolysis of tannin produces, in addition to gallic acid, some glucose or other sugars, depending upon the source of the tannin. Sucrose, starch (soluble and insoluble), and maltose were all found to be ineffective in preventing scale formation, however. Addition compounds of starch and sodium hydroxide and sodium carbonate were prepared by dissolving the starch in the soda solution and crystallizing the addition product from absolute alcohol. These addition products proved to be ineffective in scale prevention, although somewhat better than starch alone. Similar compounds of glucose and maltose were made, but were much less easily crystallized from alcohol, ice being necessary, and the products as finally obtained were too gummy to permit easy handling. An addition product of starch and gallic acid was also prepared, and when tested in the unit it prevented all but a slight scaling of the tube.

A compound of hexohexosan was prepared by heating 10 grams of starch in 100 grams of glycerol to 401 deg. F. until iodine gave a red color, then crystallizing from absolute alcohol. Trihexosan was made by heating as above until no color was obtained with iodine. The glycerine was distilled off under high vacuum, and the decolorized water solution of the residue crystallized from alcohol. Both compounds resulted in heavy scaling in the testing unit.

Bomb Tests

In order to study the effect of the decomposition, which might occur at the higher temperatures encountered in actual operation, on the organic compounds, tests were run in which solutions were first heated in sealed bombs at 360 and 540 deg. F. for 40 hours, cooled, removed from the bombs, and then tested in the regular testing apparatus. Such tests were made on pyrogallol, cutch, and starch. The bomb tests were run at three concentrations so as to make 1.25, 6.25 and 31.2 p.p.m. of the organic material being tested. All were made alkaline with 12.5 p.p.m. of sodium hydroxide.

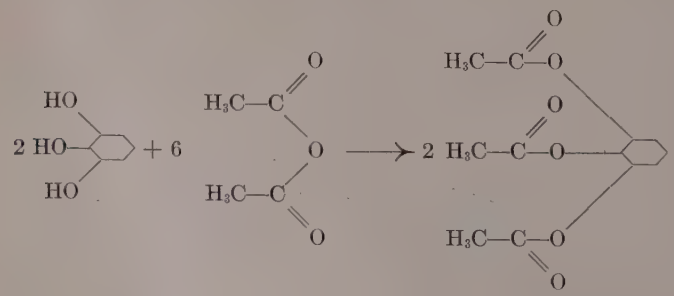
The lowest concentration (1.25 p.p.m.) resulted in the greatest scale deposition, the medium concentration (6.25 p.p.m.) in a medium amount, and the highest (31.2 p.p.m.) in the least amount of scale in all cases for pyrogallol and cutch. Samples from bombs run at 540 deg. F. showed a medium scale deposit in the testing unit for the highest concentration of cutch and pyrogallol, while those at 360 deg. F. showed only a slight scale formation.

Sodium sulphite added to the bomb tests was quite effective in preventing or delaying the complete oxidation of the pyrogallol and cutch at 360 deg. F., as was indicated by the results obtained in the testing unit. At 540 deg. F. the sodium sulphite was less effective, however.

Starch was also run in the bomb tests under the same conditions as given for pyrogallol and cutch. When run in the testing unit at 25 p.p.m. sodium hydroxide and 125 p.p.m. starch, a slight scaling resulted. Temperature had no effect. It is interesting to observe that both sodium hydroxide and starch separately have been found quite ineffective, and that the prepared addition compound of sodium hydroxide and starch was not effective.

Miscellaneous

Sodium alginate, a colloidal vegetable pentosan, was tried and found to prevent all except a slight scaling of the tube. 1:2:3 triacetoxybenzene has been prepared.



The effect of covering the OH groups of pyrogallol was expected to be shown. It was supposed also that the addition of the $CH_2C=O$ group might have a tendency to decrease the rate of oxidation. This compound changed from colorless to a light greenish brown upon being made alkaline, and a medium to small amount of grey scale resulted.

A mixture of 20 p.p.m. each of sodium carbonate, starch, and pyrogallol gave a tube almost free of scale except for small traces. Substituting glucose and then maltose for the starch, a very slight scaling was obtained. However, by using pyrogallol and sodium carbonate alone, and omitting the starch, it was found that practically all of the beneficial results were due to the alkaline pyrogallol solution.

No definite conclusions may be drawn at this stage, since the work on the oxidation of pyrogallol has not been entirely successful thus far. However, it is known that pyrogallol, after a certain length of time, does completely oxidize and break down so as to become ineffective in scale prevention. Higher temperatures favor this breakdown. The same is true of cutch. Bomb tests indicate clearly that the beneficial results of pyrogallol are due largely to its intermediate oxidation products in alkaline solution.

The materials which proved to be effective in preventing calcium sulphate scale were tested and found to also prevent calcium carbonate scale.

(2) Effect of Organic Matter on Precipitation of Calcium Carbonate at 212 deg. F.

Tests were run in order to study the effect of various organic materials on the precipitation of calcium carbonate from a bicarbonate solution on boiling, and the amount of calcium remaining in solution after boiling.

In order to study the effect of various organic materials on the solubility of calcium with respect to the time of boiling, the following type of procedure was followed:

A set of four samples to each set of organic material was weighed out into 500 cc. Erlenmeyer flasks (in duplicate for checks) to contain 20, 40, 80 and 160 p.p.m. of organic material when 250 cc. of University of Illinois tap water, the analysis of which is given in Table 59, were added to them. These samples were all refluxed for 15 minutes, clocking only the actual time of refluxing from the start of boiling. All samples were treated exactly alike in that only one person was allowed to start, time, and take off each test. After refluxing for 15 minutes, the samples were removed and filtered through

TABLE 59

RESULT OF BOILING UNIVERSITY OF ILLINOIS WATER

Test No.	Minutes Boiled	Composition After Boiling p.p.m.		
		Silica	Calcium	Magnesium
Blank	0	21.5	60.5	27.4
21	15	20.6	16.3	26.4
20	30	14.4	9.12	15.0
20	60	8.75	5.81	10.6
21	120	5.13	3.98	7.89

TABLE 60

ACTION OF PYROGALLOL ON UNIVERSITY OF ILLINOIS WATER

Test No.	Pyrogallol Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
34	20	15	21.9	26.0	25.3
30	40	15	24.6	34.0	....
30	80	15	22.1	47.2	....
30	160	15	21.3	58.6	29.3
35	20	30	15.0	21.2	24.7
31	40	30	23.9	26.0	23.5
31	80	30	23.8	35.1	28.8
31	160	30	24.3	49.3	26.1
36	20	60	17.8	17.7	17.5
32	40	60	21.0	18.9	15.6
32	80	60	23.8	28.9	20.9
32	160	60	22.7	42.9	23.0
37	20	120	19.9	12.3	8.5
33	40	120	25.7	8.8	....
33	80	120	20.2	16.2	7.2
33	160	120	24.0	21.3	11.3

TABLE 61

ACTION OF TANNIC ACID ON UNIVERSITY OF ILLINOIS WATER

Test No.	Tannic Acid Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
38	20	15	27.3	31.5	26.3
38	40	15	25.6	35.3	25.0
38	80	15	24.6	46.5	22.9
42	160	15	19.8	52.9	19.5
39	20	30	18.5	19.3	24.8
39	40	30	20.7	19.9	23.8
39	80	30	19.0	29.6	32.0
42	160	30	22.0	40.7	16.7
40	20	60	22.9	14.1	17.0
40	40	60	24.1	17.5	19.5
40	80	60	26.6	19.1	16.7
42	160	60	27.0	25.8	14.7
41	20	120	12.4	10.6	9.1
41	40	120	12.4	12.7	10.4
41	80	120	13.0	15.6	11.4
45	160	120	22.5	19.0	9.6

TABLE 62
ACTION OF CHESTNUT EXTRACT ON UNIVERSITY OF ILLINOIS WATER

Test No.	Chestnut Extract Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
34	20	15	19.5	19.5	25.5
29	40	15	20.5	26.3	28.3
29	80	15	26.9	53.1	28.3
29	160	15	26.1	60.7	31.0
35	20	30	17.3	26.0	23.0
26	40	30	21.4	18.7	22.1
26	80	30	22.8	28.7	23.9
26	160	30	25.5	26.5	21.0
36	20	60	19.2	15.6	17.9
28	40	60	16.1	11.0	14.9
28	80	60	16.0	16.8	19.0
28	160	60	20.3	21.9	19.4
37	20	120	15.2	11.1	6.2
27	40	120	29.0	8.3	7.5
27	80	120	21.1	11.2	12.4
27	160	120	19.0	14.4	9.4

TABLE 63
ACTION OF CUTCH NO. 1 ON UNIVERSITY OF ILLINOIS WATER

Test No.	Cutch Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
34	20	15	22.5	20.0	25.9
22	40	15	21.6	53.0	28.2
22	80	15	27.9	57.8	26.9
22	160	15	26.9	55.3	31.7
35	20	30	17.9	15.7	24.9
23	40	30	29.3	19.0	25.4
23	80	30	30.3	24.4	22.8
23	160	30	36.8	21.3	19.4
36	20	60	10.2	7.8	17.9
24	40	60	24.9	9.6	15.1
24	80	60	28.4	13.0	14.8
24	160	60	26.4	15.4	12.8
37	20	120	22.7	8.5	5.6
25	40	120	30.1	7.4	3.7
25	80	120	36.3	10.1	7.8
25	160	120	31.0	11.0	6.5

suction filters as quickly as possible, and then cooled. Two hundred-cc. samples were then taken and analyzed. The same procedure was carried out for periods of 30 minutes, 60 minutes, and 120 minutes on all samples.

The tests as described were carried out using pyrogallol, tannic acid, chestnut extract, cutch, gelatin, and starch. The results of these

tests are shown in Table 60. It may be seen from the table that the following inferences may be stated:

(1) The greater the concentration of pyrogallol, the more soluble the calcium. This is true in the case of every point except one (40 p.p.m. at 120 minutes).

(2) The greater the time of refluxing, the less the effect of the higher concentrations of pyrogallol: that is, if boiling or refluxing is to take place for a greater length of time than two hours, lower concentrations of pyrogallol are more effective.

Tannic Acid

The results of these analyses are shown in Table 61. The relative effectiveness for the relation of parts per million of tannic acid, time, and the solubility of calcium may be seen clearly.

(1) The greater the concentration of tannic acid, the more soluble the calcium.

(2) It appears that even over a longer period of time the higher concentrations of tannic acid might be justified as being more effective.

Chestnut Extract

The results for chestnut extract are given in Table 62, which shows the following:

(1) The lower concentrations (20 p.p.m. and 40 p.p.m.) do not hold calcium in solution very well, even after a short period of boiling.

(2) The higher concentrations (80 and 160 p.p.m.) hold calcium in solution very well, but for only a short length of time.

(3) For long periods of boiling or refluxing (1 hour or more), the lower concentrations of chestnut are probably just as effective as the higher concentrations, with the 160 p.p.m. having a slight advantage.

Cutch No. 1

Table 63, which represents the analysis of samples treated with cutch No. 1, appears to be conclusive in itself in that it shows the following:

(1) When a greater concentration than 20 p.p.m. of cutch No. 1 is used, this cutch will maintain the solubility of calcium for a short period of time. The large drop in the soluble calcium between 15 minutes and 30 minutes of refluxing makes this very apparent.

(2) Cutch No. 1 will not maintain the solubility of calcium for any length of time.

(3) The lower concentrations of cutch No. 1 are just as effective

TABLE 64
ACTION OF CUTCH NO. 2 ON UNIVERSITY OF ILLINOIS WATER

Test No.	Cutch Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
73	20	15	23.3	34.5	27.7
73	40	15	23.9	37.8	25.2
73	80	15	25.4	60.4	30.3
77	160	15	28.3	62.9	....
74	20	30	24.7	19.6	27.5
74	40	30	23.4	28.0	26.0
74	80	30	29.7	31.2	25.9
77	160	30	22.5	27.9	....
75	20	60	9.4	7.5	14.5
75	40	60	13.5	6.7	13.8
75	80	60	24.9	9.7	12.7
77	160	60	29.3	12.5	....
76	20	120	24.9	5.1	46.4
76	40	120	19.9	3.9	40.1
76	80	120	26.4	6.7	50.8
78	160	120	31.4	11.4	....

TABLE 65
ACTION OF GELATIN ON UNIVERSITY OF ILLINOIS WATER

Test No.	Gelatin Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
69	20	15	18.1	21.9	24.8
69	40	15	17.9	18.8	23.6
69	80	15	19.1	17.5	22.9
71	20	30	18.6	7.6	19.3
71	40	30	20.1	7.5	23.5
71	80	30	18.9	8.3	22.4
70	20	60	18.8	8.9	16.4
70	40	60	16.5	8.3	14.7
70	80	60	14.3	6.7	12.0
72	20	120	14.1	6.3	4.6
72	40	120	13.9	6.1	7.3
72	80	120	12.8	6.1	6.6

as the higher concentrations for maintaining the solubility of the calcium.

Cutch No. 2

The results of the tests run on cutch No. 2 are shown in Table 64, and may be summarized as follows:

(1) Cutch No. 2, when used in concentrations of greater than 80 p.p.m., is very effective in maintaining the solubility of calcium for a short period of time.

TABLE 66

ACTION OF SOLUBLE STARCH ON UNIVERSITY OF ILLINOIS WATER

Test No.	Starch Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
65	20	15	20.5	18.3	53.6
65	40	15	19.4	13.8	50.0
65	80	15	20.6	13.4	54.4
66	20	60	19.0	4.9	34.3
66	40	60	12.9	3.2	31.0
66	80	60	11.5	3.0	30.1

TABLE 67

EFFECT OF VARIOUS ORGANIC MATERIALS ON CALCIUM SOLUBILITY IN UNIVERSITY OF ILLINOIS WATER

Material Added	Minutes Boiled	Residual Calcium in p.p.m.			
		20 p.p.m. Organic	40 p.p.m. Organic	80 p.p.m. Organic	160 p.p.m. Organic
Cutch No. 2	15	34.5	37.8	60.4	62.9
Pyrogallol	15	26.0	34.0	47.2	58.6
Cutch No. 1	15	20.0	53.0	57.8	55.3
Chestnut Extract	15	19.5	26.3	53.1	28.3
Tannic Acid	15	31.5	35.3	46.5	52.9
Starch	15	18.3	13.8	13.4	....
Gelatin	15	21.9	18.8	17.5	....
Cutch No. 2	30	19.6	28.0	31.2	27.2
Pyrogallol	30	21.2	26.0	35.1	49.3
Cutch No. 1	30	15.7	19.0	24.4	21.3
Chestnut Extract	30	26.0	18.7	28.7	26.5
Tannic Acid	30	19.3	19.9	29.6	40.7
Starch	30	....	....	....	....
Gelatin	30	7.6	7.5	8.3	....
Cutch No. 2	60	7.5	6.7	9.7	12.3
Pyrogallol	60	17.7	18.9	28.9	42.9
Cutch No. 1	60	7.8	9.6	13.0	15.4
Chestnut Extract	60	15.6	11.0	16.8	21.9
Tannic Acid	60	14.1	17.5	19.1	25.8
Starch	60	4.9	3.2	3.0	....
Gelatin	60	8.9	8.3	6.7	....
Cutch No. 2	120	5.1	3.9	6.7	11.4
Pyrogallol	120	12.3	8.8	16.2	21.3
Cutch No. 1	120	8.5	7.4	10.1	11.0
Chestnut Extract	120	11.1	8.3	11.2	14.4
Tannic Acid	120	10.6	12.7	15.6	19.0
Starch	120	....	....	....	....
Gelatin	120	6.3	6.1	6.1	....
Tannic Acid	16 hrs.	....	10.4	....	11.4
Pyrogallol	16 hrs.	....	10.2	....	12.9
Chestnut Extract	16 hrs.	....	8.4	....	17.3

(2) Lower concentrations (20 p.p.m. to 40 p.p.m.) are not very effective in maintaining the solubility of calcium even for short periods of time.

(3) For a long period of time (2 hours), the higher the concentration of cutch No. 2, the greater the maintenance of the calcium solubility. Here the 160 p.p.m. is decidedly the most effective.

Gelatin

Not much need be said regarding the data obtained for the effects of gelatin, as shown in Table 65, except:

(1) Gelatin does not maintain the solubility of calcium for any length of time, or at any of the concentrations used.

Starch

Table 66 shows the results of the data obtained on starch. What is said for gelatin may also be said for starch. For this reason, the starch runs were cut short after two runs.

Summary of Solubility Tests on University of Illinois Tap Water

Tables 59 to 66 show the relationships between the various concentrations of each individual organic substance, the time of boiling, and the solubility of the calcium. Table 67 contains a combined summary of the foregoing individual studies.

It appears that the best general summary of the information contained in Table 67 may be tabulated as follows:

General Ability to Maintain Solubility of Calcium	Concentration			
	20 p.p.m.	40 p.p.m.	80 p.p.m.	160 p.p.m.
First	Pyrogallol	Pyrogallol	Pyrogallol	Pyrogallol
Second	Chestnut Extract	Tannic Acid	Tannic Acid	Tannic Acid
Third	Tannic Acid	Chestnut Extract	Chestnut Extract	Chestnut Extract
Fourth	Cutch No. 1	Cutch No. 1	Cutch No. 1	Cutch No. 2
Fifth	Cutch No. 2	Cutch No. 2	Cutch No. 2	Cutch No. 1
Sixth	Gelatin	Gelatin	Gelatin	Gelatin
Seventh	Starch	Starch	Starch	Starch

This summary may be used to express the general relationship of the compounds used, but it does not tell the whole story. It should be qualified by the following statements wherever it is referred to.

Concentration 20 Parts Per Million

(1) Pyrogallol, chestnut extract, and tannic acid are practically equally effective in maintaining the solubility of calcium, with a slightly greater effectiveness in the case of pyrogallol with time.

(2) Neither cutch No. 1 nor cutch No. 2 are very effective at this concentration. However, cutch No. 2 is slightly better for shorter periods of time, while cutch No. 1 is more effective on the long runs.

(3) Gelatin has little or no effect on the solubility of calcium.

Concentration 40 Parts Per Million

(1) At this concentration cutch No. 1 is most effective in maintaining the solubility of calcium for a short period of time.

(2) Considering a long-time run, it appears that pyrogallol, chestnut, and all the other materials except tannic acid have reached equilibrium conditions in two hours.

(3) Tannic acid, however, appears to be more effective in maintaining the solubility of calcium for periods of time longer than two hours, its equilibrium being established sometime after two hours.

(4) Gelatin has little or no effect on the solubility of calcium.

Concentration 80 Parts Per Million

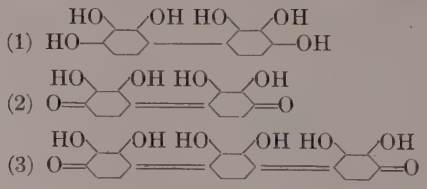
(1) Both cutches may be said to be the most effective in maintaining the solubility of calcium for a short time (less than 15 minutes).

(2) Pyrogallol exceeds all the other materials in maintaining the solubility of the calcium for periods of from 30 to 120 minutes, but the results do not seem to indicate that it would be most effective over runs of longer duration. In this respect the results would indicate that tannic acid had a decided advantage over pyrogallol for a time greater than two hours.

(3) Gelatin has no effect on the solubility of calcium.

Effect of Passing Air Free From Carbon Dioxide Into Samples During Refluxing with Pyrogallol

It is known that pyrogallol, in the presence of dilute alkali, oxidizes into compounds reported to be of the following nature:



A test was run to determine whether or not the oxidation by ordinary bubbling of air free from carbon dioxide through the water at the time of refluxing would have any effect on the "holding up" power of pyrogallol. The test was carried out exactly as all other

TABLE 68
COMPARISON OF ACTION OF PYROGALLOL IN PRESENCE OF AND IN ABSENCE OF AIR ON UNIVERSITY OF ILLINOIS WATER

Test No.	Pyrogallol Added p.p.m.	Minutes Boiled	Residual Calcium, p.p.m.	
			Without Air	With Air
32-44	40	60	17.7	13.2
32-44	80	60	18.9	20.3
32-44	160	60	28.9	24.0

tests had been, except for the bubbling of air through the water during refluxing. The results of this test are compared with those of a test carried out without air oxidation in Table 68.

It can be seen from Table 68 that, when pyrogallol is oxidized by air during the time of refluxing, there is a tendency for less calcium to be held in solution. In the case of the 40 parts per million and the 160 parts per million runs, the actual difference in amount of calcium held in solution was about 5 parts per million (less) when air was passed in. In the case of the 80 parts per million test, no inference at all can be made, due to the fact that the accuracy of the analytical procedure is not greater than $\pm$ 1 part per million. However, the 40 and the 160 parts per million runs do show that oxidation of pyrogallol does tend to decrease its property of holding calcium in solution. It is evident also from this (though enough evidence is not presented here) that it is either pyrogallol itself, or at least one of its first oxidation products, such as

that tends to hold the calcium in solution, and that the more highly oxidized derivatives of pyrogallol should be less efficient in increasing the solubility of calcium.

Ability of Pyrogallol to Maintain the Solubility of Calcium

In order to determine whether or not the addition of pyrogallol to a sample of water which had refluxed a definite time would either increase the solubility of the calcium with further boiling, or at least maintain the solubility of the calcium at the same value as when the pyrogallol was added, the following test was made.

Two samples of water were refluxed for 15 minutes, the time being checked as closely as possible to the half minute. At this point 40

parts per million of pyrogallol were added, the one sample being allowed to reflux for 15 minutes longer, then filtered immediately and cooled, and the other being refluxed for 105 minutes longer, and then immediately cooled. The results of the analysis, as compared with those from a blank and from a test where pyrogallol was added at the beginning of each run, are shown in Table 69.

From the table it will be seen that the pyrogallol does not tend to increase the solubility of the calcium or to dissolve any calcium already precipitated by refluxing, but that it does tend to maintain the solubility of the calcium where it picks it up, so that after a 120-minute run the soluble calcium is approximately the same whether pyrogallol is added at the start or after 15 minutes of refluxing. Where no pyrogallol was added in 15 minutes of refluxing the soluble calcium dropped from 60.5 parts per million to 16.3 parts per million. When pyrogallol was added at this point, it tended to maintain the calcium in solution so that, at 120 minutes, the soluble calcium was 9.5 parts per million, which is approximately equivalent to the amount present (8.8 p.p.m.) after 120 minutes when pyrogallol was added at the beginning of the run.

After running the tests as shown in Tables 59 to 66, it was decided that the pH values of the different runs should be obtained in order to determine whether or not the organic matter was retarding the increase in pH value, and thus affecting the solubility of the calcium. It will be noted from Table 70 that there is a slight increase in the pH with time of refluxing, the increase being slightly greater when only 40 parts per million of organic matter was added. The fact that 160 parts per million of organic matter gives less variation in pH value is naturally what would be expected from the nature of the structure of the constituents of these materials. Even in the case of the greatest variation in pH with refluxing in the presence of organic material, the change is less than the variation with refluxing in the absence of organic matter. The total variations also are so small that it may be definitely stated that the organic matter is not affecting the solubility of the calcium by retarding the change in pH value.

Effect of Various Concentrations of Organic Materials With Time on the Solubility of Calcium in Taylorville City Water

The previous portion of this report deals with the relative effectiveness of various organic materials in maintaining the solubility of calcium in University of Illinois tap water. The following data deal with the same type of experimentation, using the same procedure, on

TABLE 69

EFFECTIVENESS OF PYROGALLOL IN MAINTAINING SOLUBILITY OF CALCIUM IN UNIVERSITY OF ILLINOIS WATER

Test No.	Pyrogallol Added p.p.m.	Time of Refluxing Before Addition of Pyrogallol min.	Time of Refluxing After Addition of Pyrogallol min.	Total Time min.	Residual Calcium p.p.m.
21	..	..	..	..	60.5
21	..	..	..	15	16.3
20	..	..	..	30	9.1
21	..	..	..	120	3.9
30	40	..	15	15	34.0
31	40	..	30	30	26.0
33	40	..	120	120	8.8
43	40	15	15	30	11.8
43	40	15	105	120	9.5

TABLE 70

EFFECT OF ADDITION OF ORGANIC COMPOUNDS AND TIME OF BOILING ON pH VALUE OF UNIVERSITY OF ILLINOIS WATER

Organic Material Added	Material Added p.p.m.	pH Value After 15 min. Refluxing	pH Value After 60 min. Refluxing	pH Value After 120 min. Refluxing
None	...	8.9	9.6	9.8
Chestnut Extract	40	9.2	9.5	9.6
	160	8.9	9.4	9.6
Cutch	40	9.1	9.3	9.6
	160	9.2	9.5	9.4
Pyrogallol	40	9.3	9.5	9.3
	160	9.2	9.0	9.0

TABLE 71

RESULTS OF BOILING TAYLORVILLE CITY WATER

Test No.	Minutes Boiled	Composition After Boiling, p.p.m.		
		Silica	Calcium	Magnesium
50	...	23.6	189.2	73.5
56	15	27.6	95.1	66.4
56	60	23.5	67.6	66.6
56	120	24.5	70.8	64.4

Note: Total sulphate = 443 p.p.m. SO_4.

TABLE 72
ACTION OF PYROGALLOL ON TAYLORVILLE CITY WATER

Test No.	Pyrogallol Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
57	20	15	26.6	138.5	71.7
57	40	15	27.8	131.3	70.5
57	80	15	30.2	140.0	71.5
60	160	15	27.3	163.0	65.3
58	20	60	24.8	97.5	75.7
58	40	60	24.8	104.0	64.5
58	80	60	22.8	116.0	67.0
60	160	60	26.5	143.0	63.8
59	20	120	29.7	93.5	68.2
59	40	120	27.0	101.0	65.0
59	80	120	30.7	119.0	61.9
60	160	120	29.5	131.5	55.0

TABLE 73
ACTION OF CUTCH NO. 1 ON TAYLORVILLE CITY WATER

Test No.	Cutch Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
61	20	15	30.5	130.9	....
61	40	15	28.8	149.5	....
61	80	15	27.5	149.0	....
64	160	15	20.3	145.0	63.7
62	20	60	20.3	95.3	67.4
62	40	60	18.8	107.4	63.9
62	80	60	31.2	112.3	61.0
64	160	60	27.0	116.5	53.8
63	20	120	23.5	87.9	58.5
63	40	120	23.3	97.6	55.6
63	80	120	22.8	105.8	53.3
64	160	120	24.5	117.2	44.2

TABLE 74
ACTION OF SOLUBLE STARCH ON TAYLORVILLE CITY WATER

Test No.	Starch Added p.p.m.	Minutes Boiled	Composition After Boiling, p.p.m.		
			Silica	Calcium	Magnesium
67	20	15	30.0	72.3	73.4
67	40	15	29.0	73.1	74.9
67	80	15	32.3	71.0	75.8
68	20	60	22.3	88.7	71.6
68	40	60	22.0	78.7	67.3
68	80	60	23.0	75.7	72.0

Taylorville City water, a water high in calcium and sulphate. Table 71 shows the results of boiling this water.

It can be seen from this table that soluble calcium in the unboiled water is very high (189.2 p.p.m.), and that the sulphate is exceedingly high (443 p.p.m. SO_4). The table also shows that, after one hour of refluxing, the solubility of the calcium apparently reached a minimum value for the time of refluxing of this experiment, and with longer heating the indications are that in this water the solubility of the calcium would remain at about 70 parts per million.

Tests on this water were run in exactly the same manner as in the case of University water, using pyrogallol, cutch, and starch. The results of the various concentrations of these tests are shown in Tables 72, 73, and 74. These may be summarized as follows:

Pyrogallol

(1) In all cases it appears that the higher the concentration of pyrogallol, the higher the solubility of calcium.

(2) The efficiency of a concentration of 160 parts per million of pyrogallol in maintaining the solubility of calcium appears to warrant its use, even over long periods of time.

(3) Twenty parts per million of pyrogallol are almost as effective as 40 parts per million.

(4) The relationship of the concentration of pyrogallol to its effectiveness in maintaining the solubility of calcium in Taylorville water is somewhat analogous to the similar relationship for University water.

Cutch No. 1

(1) For a short period of time (15 minutes), it appears that all concentrations of cutch No. 1 above 20 parts per million (that is, 40 parts per million, 80 parts per million, and 160 parts per million) are equally effective in maintaining the solubility of calcium.

(2) As the time increases, a direct relationship is shown between the concentrations of cutch No. 1 and the solubility of calcium.

(3) The effect of cutch No. 1 on Taylorville water is analogous to its effect on University water.

Soluble Starch

(1) Starch is inefficient in maintaining the solubility of calcium.

(2) Its action in the case of Taylorville water is similar to its action in the case of University water.

TABLE 75
EFFECT OF VARIOUS ORGANIC MATERIALS ON CALCIUM SOLUBILITY IN TAYLORVILLE CITY WATER

Organic Material Added	Minutes Boiled	Residual Calcium in p.p.m.				
		0 p.p.m. Organic	20 p.p.m. Organic	40 p.p.m. Organic	80 p.p.m. Organic	160 p.p.m. Organic
Blank	0	189.2	....	....	....	....
Blank	15	95.1	....	....	....	....
Pyrogallol	15	....	138.5	131.3	140.0	163.0
Cutch	15	....	130.9	149.5	149.0	145.0
Starch	15	....	72.3	73.1	71.0	....
Blank	60	67.6	....	....	....	....
Pyrogallol	60	....	97.5	104.0	116.0	143.0
Cutch	60	....	95.3	107.4	112.3	116.5
Starch	60	....	88.7	78.7	75.7	....
Blank	120	70.8	....	....	....	....
Pyrogallol	120	....	93.5	101.0	119.0	131.5
Cutch	120	....	87.9	97.6	105.8	117.2
Starch	120	....	....	....	....	....

Conclusions from Taylorville Water Results

Just as in the case of Table 67 for University of Illinois water, Table 75 shows a combined summary of the results with Taylorville water, in order to present a comparison of the effectiveness of pyrogallol and cutch in maintaining the solubility of calcium at each concentration.

Concentration 20 Parts Per Million

Table 75 shows the relative effectiveness of cutch and pyrogallol at a concentration of 20 parts per million to be as follows:

(1) Cutch and pyrogallol at this concentration are about equally effective in maintaining the solubility of calcium, pyrogallol being slightly more effective.

Concentration 40 Parts Per Million

Table 75 presents a comparison of the relative effectiveness of pyrogallol and cutch at this concentration, which may be stated as follows:

(1) At this concentration apparently cutch No. 1 is slightly more effective for shorter periods of time, while for runs of long duration pyrogallol would be more effective in maintaining the solubility of calcium.

Concentration 80 Parts Per Million

Table 75 compares pyrogallol and cutch at this concentration; from the data presented the following conclusion may be drawn:

(1) As in the foregoing, here also it appears that cutch No. 1 is slightly more effective at this concentration for shorter periods of time, while for long runs pyrogallol is more effective in maintaining the solubility of calcium.

Concentration 160 Parts Per Million

Table 75 shows a decided difference from all the previous comparisons as to effectiveness in that

(1) Pyrogallol is more effective than cutch No. 1 at this concentration, for runs of either short or long duration.

As a general summary of the foregoing comparison, the following table may be of some help. It must be remembered, however, that any individual comparison where the same concentrations are compared must be considered in connection with this chart. Starch in all cases appeared to give results comparable to those of a blank.

General Ability to Maintain Solubility of Calcium	Concentration			
	20 p.p.m.	40 p.p.m.	80 p.p.m.	160 p.p.m.
First	Pyrogallol	Cutch No. 1	Pyrogallol	Pyrogallol
Second	Cutch No. 1	Pyrogallol	Cutch No. 1	Cutch No. 1
Negative	Starch	Starch	.....	.....

In considering the hypothetical combinations in the preceding table, it will be seen that, on refluxing, the calcium content of Taylorville water should never fall below 61 parts per million. This is due to the fact that this calcium is combined as calcium sulphate, the solubility of which is not decreased to a point of precipitation at the temperature used. It will be interesting to note that at all times when the organic materials were added, the lowest calcium content never fell to this value, but was always much above it. It will also be noted from the experimental evidence that this low calcium value was more closely approached with starch and gelatin than with any of the other organic materials tested.

Generalized Conclusions

Inasmuch as this entire report is made up of individual conclusions drawn from individual experimental data, it might be advisable to make the following generalized conclusions:

(1) With all the organic compounds tried the soluble calcium decreased with time of boiling.

Table 76
Analysis of Taylorville City Water

Calcium	190 p.p.m.
Magnesium	68 p.p.m.
Total Alkalinity as $CaCO_3$	323 p.p.m.
Total Sulphate	443 p.p.m.
Hypothetical Combination	
Calcium Carbonate	323 p.p.m.
Calcium Sulphate	207 p.p.m.
Magnesium Sulphate	340 p.p.m.
Sodium Sulphate	37 p.p.m.

(2) With all the organic compounds run for different lengths of time, the soluble calcium increased with an increase in organic matter.

(3) Pyrogallol was most effective in maintaining the solubility of calcium for periods of no longer than two hours.

(4) For periods of time of two hours or longer, tannic acid was the most effective compound to use to maintain the solubility of calcium.

(5) For maintaining the solubility of calcium for short periods of time (15 minutes), cutch No. 1 and No. 2 were effective when used in concentrations of greater than 40 parts per million.

(6) Neither starch nor gelatin was effective in maintaining the solubility of calcium above that of a blank.

(7) The organic materials, in order of decreasing effectiveness in maintaining the solubility of calcium, may be given as follows: pyrogallol, tannic acid, chestnut extract, cutch No. 1, cutch No. 2, gelatin, and starch.

(8) Oxidation of pyrogallol by means of air during refluxing apparently decreases the effectiveness of the pyrogallol in maintaining the solubility of calcium.

(9) On ultimate refluxing, an ultimate equilibrium would be established whereby the soluble calcium would approach the value for a blank. This equilibrium is reached after different periods of time, depending upon the organic material used.

(10) Pyrogallol, when added to a solution after a definite amount of calcium has been precipitated, tends to maintain the solubility of calcium where it picks it up, but does not tend to redissolve any of the precipitated calcium.

(11) The relative change in pH, which occurs during refluxing and precipitation of calcium carbonate in the presence of organic material, is so slight that its effect on the solubility of calcium would be negligible.

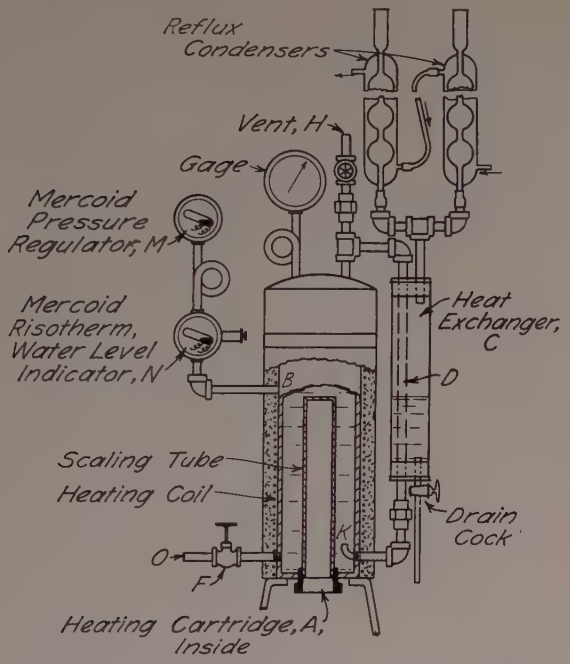


FIG. 14. APPARATUS USED FOR SCALE PREVENTION TESTS

(12) The effect of organic material in maintaining the solubility of calcium in a high-calcium, high-sulphate water (Taylorville water) is comparable to its effect in the case of a low-calcium, low-sulphate (University) water.

(B) Tests in Scaling Boiler

(1) Calcium Sulphate Scale Tests

In order to study the effect of the organic materials on scale prevention in boilers, a small stationary boiler having a capacity of three liters, a continual heat take-off, and condensate return, was designed and constructed of high pressure material. The arrangement of this experimental unit is shown in Fig. 14. The radiation was calculated at 650 B.t.u. per hour and a corresponding heat input was arranged by winding 75 ft. of No. 18 Chromel wire about the outer shell of the boiler, this heating coil operating on a 110-volt line. The main heating coil *A*, a 1.1 kw. General Electric heating cartridge, was placed in parallel with the radiation winding and carried a total of 10 amperes. In series with this heating coil was placed a Mercoid pressure control *M* and a Risotherm *N* which controlled the temperature within the

boiler. By operating the boiler so that the water level was above the point *B*, the rate of transfer of heat through the water and then to the Risotherm was not sufficient to break the circuit. When the water level fell below the point *B*, the rate of transfer of heat due to more rapid diffusion through the steam was sufficient to cause the Risotherm to break the circuit with the main heating coil.

The pressure was controlled by a Mercoid gage which broke the circuit, sending the current through a resistance when the pressure became more than that determined by the setting. The radiation coils were divided into 75 and 25 ft. sections so that additional heat could be supplied when bringing the boiler up to pressure.

Heat was continually removed from the boiler through the heat exchange *C*, which consisted of a glass tube sealed about the pipe *D*, which led from the top of the boiler back into the bottom. The pipe then acted as a take off and return. The amount of heat taken out of the boiler was determined by the amount of water present in the heat exchanger, which was arranged so that the water could be condensed in and returned to the system. The exchanger and condenser were in no way connected with the boiler internally, and were operated at atmospheric pressure. The valve *F* acted as a blow valve. A high pressure needle valve and union were placed at *H* so as to be able to blow any air from the boiler, and also to decrease condensation within the boiler after operation had ceased. The tube *K* was placed in the return so as to direct the cold feed up and away from the heating coil so that it would have no effect on the scale formation.

Method of Running Tests

The boiler water was charged into the unit through a long pipe which extended well above the boiler and which was connected at *O*. All solid material was washed down through a funnel at *H*, then the valve *F* was closed and the union at *H* replaced. It required about 30 minutes to bring the boiler up to 200 lb. per sq. in. gage pressure. When this pressure was attained the low heat was turned on and water placed in the heat exchange. The Mercoid control then held the pressure at from 250 to 275 lb. per sq. in. gage, and the boiler was operated 46 hours.

An extensive series of tests was first run in which the concentrations were from 250 to 1000 p.p.m. calcium sulphate, 3 millimoles per liter sodium hydroxide, 1000 p.p.m. sodium sulphate, and 60 p.p.m. sodium chloride. Two solutions were made of identical composition except for the calcium sulphate concentration. Solution No. 1 contained no calcium sulphate, while Solution No. 3 contained 1000 p.p.m.

calcium sulphate. Thus, by adding proportional amounts, the final solution contained the former concentrations.

In the second series of tests, it was desired to change the alkalinity from 1 to 6 millimoles per liter. Thus the feed make-up was changed. Separate solutions of calcium sulphate 1000 p.p.m. (No. 1), sodium sulphate 4000 p.p.m. (No. 4), sodium chloride 1200 p.p.m. (No. 6), and sodium hydroxide 120 millimoles per liter (No. 5) were prepared. Thus, by taking 1000 cc. No. 1, 500 cc. No. 4, 100 cc. No. 6, and 100 cc. No. 5, and adding 300 cc. of distilled water, a final solution was obtained containing 500 p.p.m. calcium sulphate, 1000 p.p.m. sodium sulphate, 60 p.p.m. sodium chloride, and 6 millimoles per liter of sodium hydroxide. At the same time as the feed was prepared, a blank was made using the same concentration, and then analyzed so as to have a check on the concentrations added to the boiler.

Table 77 shows the results of the tests made using various compounds in the small laboratory test unit at 212 deg. F. The column in the table headed "Tannin" refers to tannic acid; the term "tannic acid" as commonly used refers to gallotannin. Gallotannin has no scale-inhibiting properties. Tests using gallotannin as an inhibitor failed to show beneficial results, either in the small testing unit or in the pressure boilers. Chestnut tannin, however, is a decided inhibitor. This tannin belongs to the class of tannins known as phlobatannins. Chemically, the phlobatannin is decidedly different from the gallotannin. While the chestnut tannin, which is a typical phlobatannin, has scale-inhibiting properties, it is found that hemlock tannin, which also falls in the same class (known as phlobatannins), is not an inhibitor. Since the chemical structure of chestnut tannin and hemlock tannin are very similar, it is difficult to account for this difference in inhibiting power.

Several nitro phenolic compounds and other miscellaneous compounds were tested in the course of this investigation. The results of these tests are shown in Table 77.

Many of the compounds listed in the table gave good results when tested in the small laboratory test unit. Many of these compounds, however, when used in the test boilers failed to show scale-inhibiting properties. The pressure maintained by the boilers was 275 lb. per sq. in.; the length of each test run was approximately 48 hrs.; and the calcium sulphate concentration was usually in the region of 500 parts per million. Since these compounds failed to show beneficial results under these conditions, they were temporarily abandoned.

Several commercial preparations were then tried in an effort to find something that would have scale-inhibiting properties under the

Table 77

Calcium Sulphate Scale Studies

Inhibitors used in preventing scale in laboratory tests at 212 deg. F.
Solutions used were saturated with calcium sulphate at 70 deg. F.

Blank	Scale	Tannin	Scale	Pyrogallol	Scale	Cutch	Scale	Chestnut	Scale	Gallates	Scale
Also saturated with calcium carbonate	Medium	Tannic acid 15 p.p.m.	Slight	Pyrogallol 10 p.p.m.	Very slight	Cutch Chart I (2)	Very slight	Chestnut tannin	Slight	Gallic acid	No scale, discolor
Blank	Medium	Tannic acid 10 p.p.m.	Heavy	Pyrogallol 10 p.p.m.	Slight	Cutch Chart III (2)	Very slight	Chestnut tannin	Slight to medium	Butyl gallate	Very slight
Blank	Heavy	Tannic acid 5 p.p.m.	Heavy	Pyrogallol 5 p.p.m.	Slight	Cutch Chart I (1)	Medium	Bromine precipitate from chestnut	Slight to medium	Methyl gallate 30 p.p.m.	Very slight
				Pyrogallol Sodium sulphate Sodium chloride Sodium hydroxide	Medium	Cutch non tannin residue	Medium to heavy	Gelatin precipitate from chestnut	Medium	Methyl gallate 10 p.p.m.	Very slight
				Pyrogallol Sodium sulphate Sodium hydroxide Sodium chloride	Medium	Cutch Phlobophene	Heavy (red)	Chestnut filtrate after calcium sulphate precipitation	Medium (firm)	Methyl gallate 5 p.p.m.	Slight
								Ferric chloride precipitate from chestnut	Heavy		

TABLE 77 (CONCLUDED)

CALCIUM SULPHATE SCALE STUDIES

Inhibitors used in preventing scale in laboratory tests at 212 deg. F.
Solutions used were saturated with calcium sulphate at 70 deg. F.

Hemlock	Scale	Nitro	Scale	Nitro	Scale	Nitro	Scale	Miscellaneous	Scale	Miscellaneous	Scale
Hemlock extract	Very slight	Nitro methane	Medium	Nitro pyrogallol	Very slight	Tri-nitro toluene 50 p.p.m.	Slight to medium	2-4 dinitro inaphthol sulfanic acid	Medium	Rochelle salts	Very heavy
Japonic	Slight	Para-nitro phenol	Slight	Picric acid	Very slight	Tri-nitro toluene 100 p.p.m.	Slight to heavy	Gardinol 30 p.p.m.	Medium	Thio phenol	Very heavy
Japonic phloba-tannin	Medium to heavy	Ortho-nitro phenol	Medium	Picric acid + calcium carbonate	Medium	Para-nitro toluene	Medium	Di-nitro salicylic acid	Medium (corro-sion)	Butyl sulfone	Very heavy
Tea tannin	Slight to medium	2-4 di-nitro phenol	Medium	Otho-chloro-nitro benzene	Slight (un-even)			α nitro β naphthol	Medium (flaky)		
Quercetin	Medium	Nitro hydro-quinone	Medium	Tri-nitro benzene	Slight corrosion			Phthalimide	Heavy		
				Para-nitro benzoic acid	Heavy			Sodium benzene sulfonate	Heavy		
				2-4 di-nitro toluene	Slight to medium						

TABLE 78

RELATIVE SCALE-INHIBITING EFFECT OF THE DIFFERENT SOLUBILITY FRACTIONS OF THE NATURAL PRODUCTS

Roman numerals refer to charts; the numbers in parentheses refer to fractions (see pp. 93-96)

Decreasing inhibiting power ↓	I	II	III	IV	V	VI	VII	VIII
	(4) - (5)	(2) - (4)	(1)	(1) - (3)	(2)	(1)	(1)	(1)
		(1) - (3)	(4)	(1) - (4) - (6)	(1)	(3)		
			(2) - (3)					

operating conditions of the boiler. Some of the commercial preparations tried were the following: cutch No. 1, No. 2, and No. 3, chestnut extract, hemlock extract, japonic, chesaco extract, and tannic acid. Of this series of commercial products cutch No. 1 was found to give the best results. Chestnut extract showed very decidedly scale-inhibiting properties, but was not comparable with the previously mentioned products. The remaining products were entirely without noticeable scale-inhibiting properties.

Since all of these materials are mixtures of many organic compounds, as is easily determined by their solubility behavior, attempts were made to isolate from the most effective product the chemical constituent responsible for the scale-inhibiting properties of the product. As a first attempt in this direction, a separation of the product into fractions was attempted. In this manner it was hoped to obtain a fraction which would be a concentrate of the compound or compounds responsible for scale inhibition. Separations, on the basis of the solubility of the different ingredients, were tried. The different methods of separation tried are shown by the accompanying charts. The various fractions were tested in the boilers under the conditions previously specified. The results of these boiler tests are shown in Table 78.

From Table 78 it is seen that the methods of separation used in Charts II, III, IV, V and VI have definitely proven that certain components of these mixtures have no part in the scale-prevention property shown by the product. While the active constituent of the mixtures has not yet been isolated, this table shows that at least a partial separation of the unnecessary components of the mixture has been accomplished.

The natural tannin extracts are mixtures of several organic compounds, as is evident from an examination of the literature on tanning materials. In view of this, an attempt was made to obtain the pure

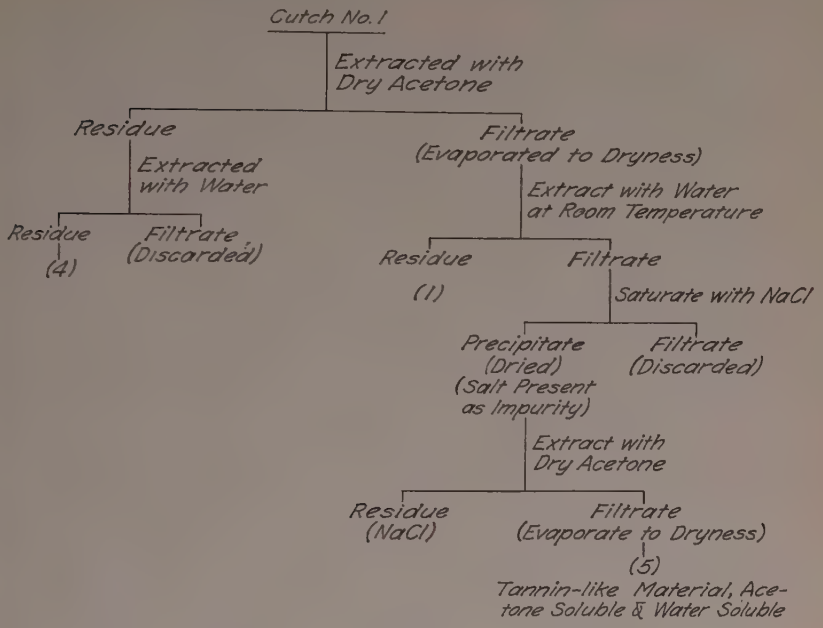


CHART I

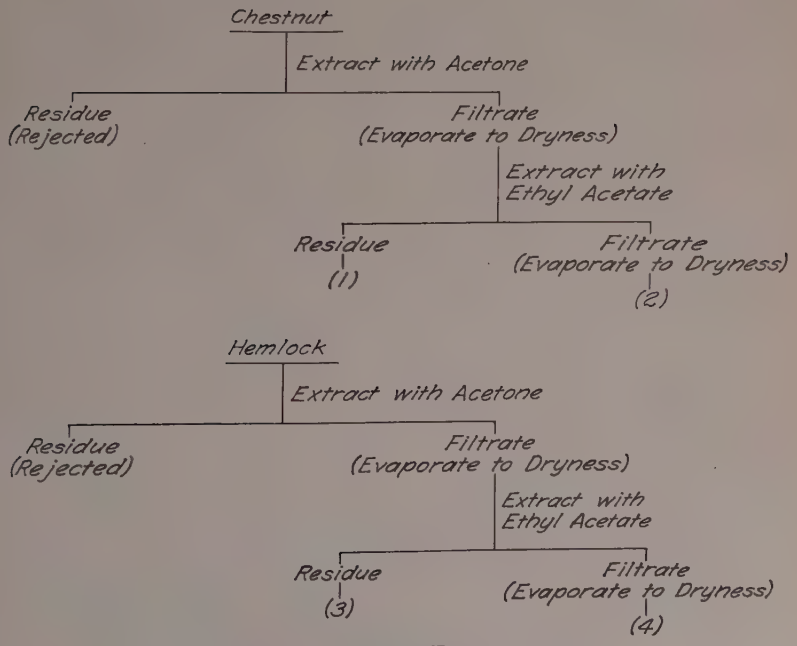


CHART II

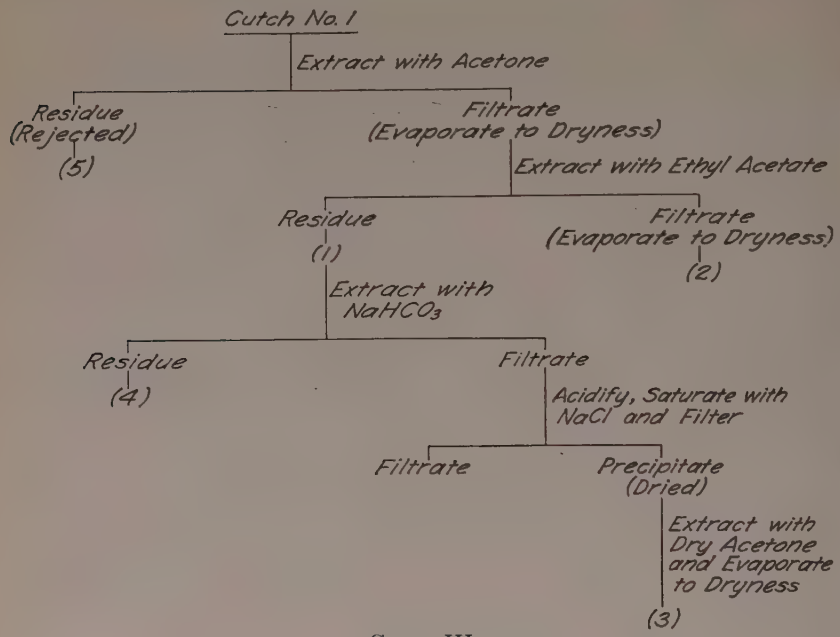
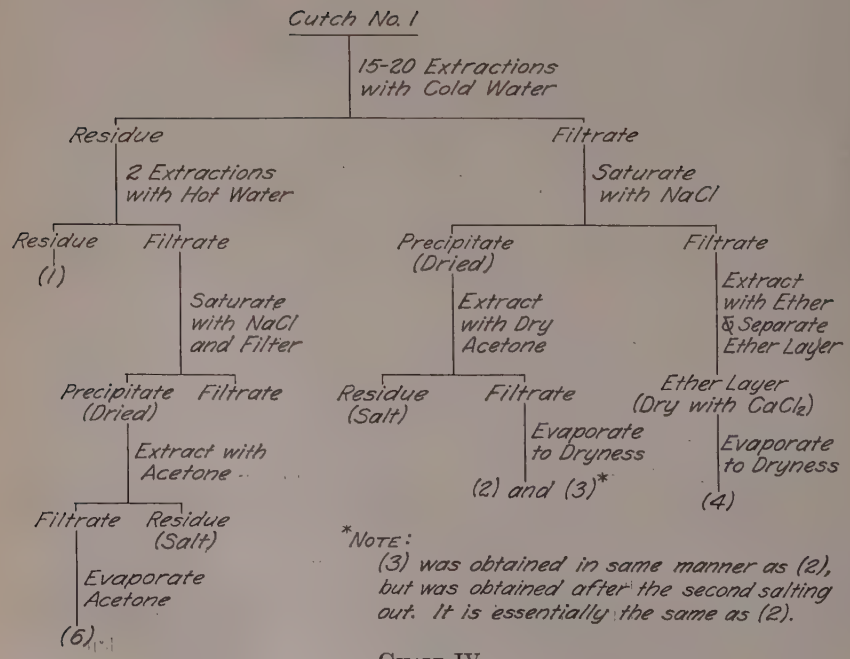


CHART III



*NOTE:
(3) was obtained in same manner as (2), but was obtained after the second salting out. It is essentially the same as (2).

CHART IV

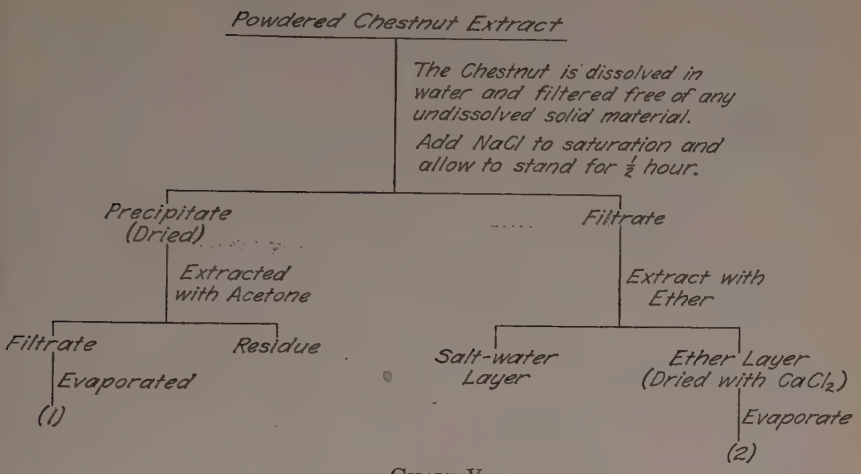


CHART V

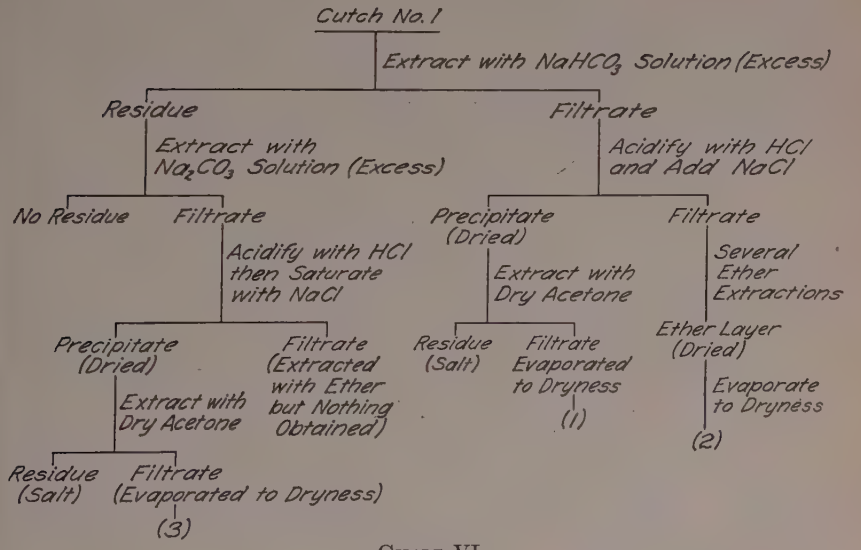
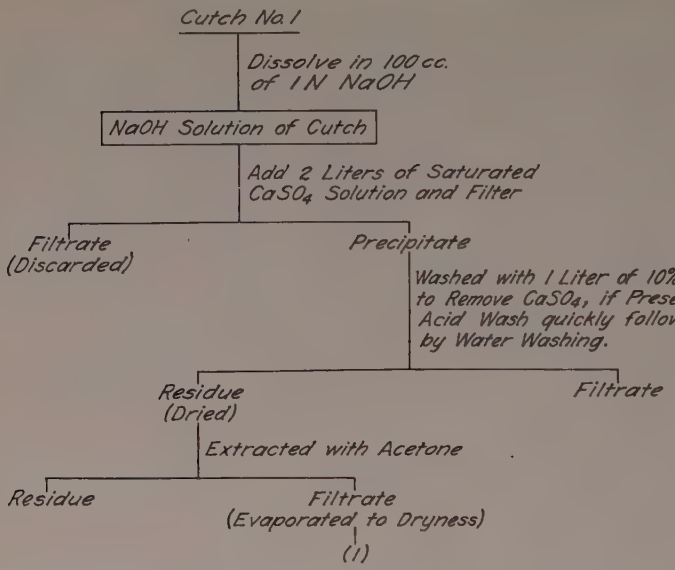


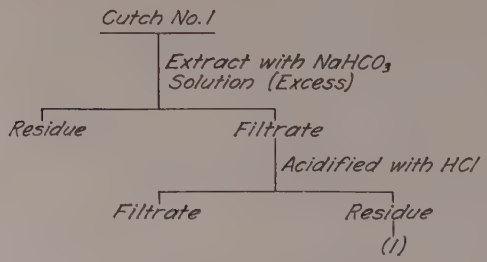
CHART VI

tannins free from other organic matter. Throughout the several separations the aim had been to isolate pure chemical individuals and study their scale-inhibiting properties. Some success had been realized from following this procedure. Eventually this course of investigation was dropped, because the similarity of the organic compounds in these mixtures is so marked that separation of them on


Cutch No. 1
Dissolve in 100 cc. of 1 N NaOH
NaOH Solution of Cutch
Add 2 Liters of Saturated $CaSO_4$ Solution and Filter
Filtrate (Discarded)
Precipitate
Washed with 1 Liter of 10% HCl to Remove $CaSO_4$, if Present. Acid Wash quickly followed by Water Washing.
Residue (Dried)
Filtrate
Extracted with Acetone
Residue
Filtrate (Evaporated to Dryness)
(1)

This chart is not a separation. This procedure was used to regenerate the cutch from the sludge thrown down when a saturated solution of calcium sulphate containing cutch is made alkaline. The object was to determine, if possible, if the scale-inhibiting properties were connected with sludge formation.

CHART VII



NOTE: *This chart was made to obtain the fraction (1) which was not isolated in Chart VI.*

CHART VIII

the basis of a difference of solubility towards organic solvents was not decided enough to give clear cut separations.

Dr. Alfred Russell has expressed the opinion that the scale-inhibiting property of the tannin is dependent upon the astringent nature of the tannin. Furthermore, it was his opinion that the iron-greening and iron-blueing property, or the ability of the tannins to form iron

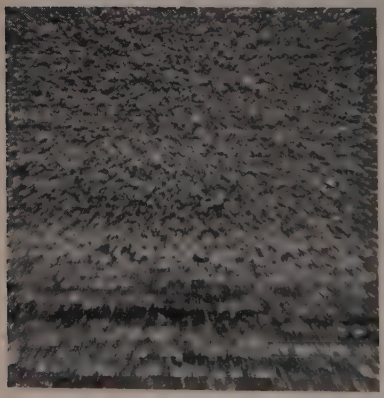
TABLE 79
EFFECT OF ASTRINGENCY ON SCALE PREVENTION

Fractions Tested	Condition of Tube After Test	Concentration of $CaSO_4$ p.p.m.		Total Alkalinity Expressed in Millimoles Per Liter of NaOH	
		At Start	At End	Before	After
Chart VI—(1) $NaHCO_3$ (astringent)	Little better than indifferent	500	27	1.9	4.2
Chart VI—(3) Na_2CO_3 (less astringent)	Indifferent	500	52	1.9	0.8
Original Cutch No. 1	Fair	500	8	2.4	1.7
Original Cutch No. 1	Fair	500	43	2.4	0.9
Chart VIII—(1) $NaHCO_3$	Indifferent	500	61	1.9	1.5

Note: The method of sampling the discharge water is responsible for the variation of $CaSO_4$ found in solution at the end of a test. The analysis merely serves to emphasize that an initial concentration of 500 p.p.m. of $CaSO_4$ is present, and that at the end of a test the $CaSO_4$ in solution is from 40 to 80 p.p.m., approximately. Therefore, it emphasizes the fact that about 400 p.p.m. of calcium are removed from solution during the test.

Pyrogallol at
low alkalinity
Good

Cutch No. 1 at
low alkalinity
Good



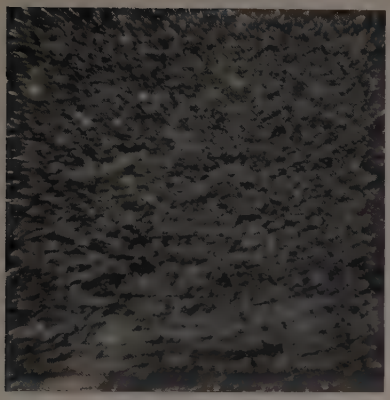
Pyrogallol at
high alkalinity
Indifferent

Cutch No. 1 at
high alkalinity
Fair

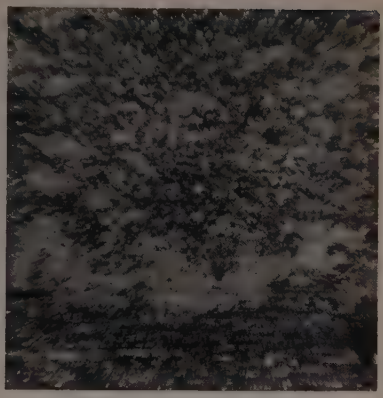
FIG. 15-a. PHOTOMICROGRAPHS OF SCALE FORMED
20 x

tannates, was in some way connected with the scale-inhibiting property of the tannin. An iron tube permitted to stand in a tannin solution, even though alkaline, will form on its surface a dark film which readily sloughs off with rubbing. This attack on the iron by the tannin is very slight, and could not possibly be injurious to the boiler tubes. Considerable experimental evidence in favor of this speculation has been obtained.

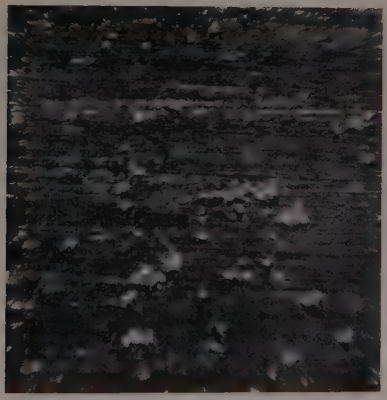
At first, the extraction of the more astringent or acidic fraction was tried. This could only be tried on cutch No. 1, since it is the



Blank at high alkalinity
Indifferent



Blank at low alkalinity
Indifferent



Pyrogallol + phenylenediamine
(Alkalinity maintained with phenylenediamine)
Good

FIG. 15-b. PHOTOMICROGRAPHS OF SCALE FORMED
20 x

only one of the natural extracts under discussion that has a sufficiently low solubility in water to make such a separation feasible. The procedure followed is outlined in Chart VI. The results obtained were not decisive enough to be depended upon. The various fractions obtained are tabulated in Table 79. An examination of this table shows that the more acidic portion of the extract and the less acidic portion have practically the same scale-inhibiting properties.

The astringent effect of the tannin can also be emphasized by lowering the alkalinity of the boiler feed water, and this accomplishes

TABLE 80
EFFECT OF ALKALINITY ON ACTION OF ORGANIC MATERIALS IN PREVENTING SCALE

Inhibitor Tested	Condition of Tube After Test	Concentration of $CaSO_4$ p.p.m.		Total Alkalinity Expressed in Millimoles Per Liter of NaOH	
		At Start	At End	Before	After
Pyrogallol	Good	500	70.7	0.5	Alk.
Pyrogallol	Indifferent (no good)	500	91.0	6.0	3.4
Cutch No. 1	Good	500	70.7	0.5	Alk.
Cutch No. 1	Indifferent (no good)	500	67.5	6.0	4.1
Catechol	Indifferent (no good)	500	64.1	3.0	1.4
Catechol	Fair	500	33.8	0.5	0.2
Hydroquinone	Indifferent (no good)	500	77.6	0.5	0.1
Hydroquinone	Indifferent (no good)	500	71.0	3.0	0.9

the effect unsuccessfully sought after in these separations. When the alkalinity of the boiler feed water is lowered, the astringent nature of the tannin will necessarily become more decided. The alkalinity of the feed water was lowered from 3 millimoles per liter to 0.5 millimoles per liter; Table 80 shows the results obtained. Reference to Fig. 15 and to Table 80 shows the vast improvement effected when the astringent property of the tannin is not repressed by alkalinity. The blank pictures are inserted for comparison. While sufficient time has not been available to run tests on the entire series of these tannins at the lower alkalinity, it seems safe to assume that they will all act in this same manner.

Purification of Tannins and Isolation of Catechin

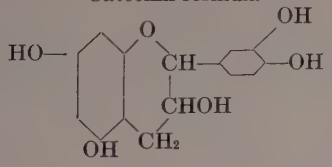
It has been previously mentioned that isolation of pure chemical individuals from these natural extracts was attempted in order to discover what was responsible for the scale-inhibiting effects obtained. The crystalline principle of cutch in catechu is reported in the literature to be catechin. Therefore, the commercial preparations called cutch probably contain a certain amount of catechin. For instance, quoting from "The Natural Organic Coloring Matters" by A. G. Perkin and G. E. Everst, pages 463 and 444, "There are several varieties of Catechu or Cutch bearing different names, according to the country or plants from which they are obtained. The following are those principally employed by dyers and tanners: Gambier Catechu; Bengal or Acacia Catechu; Bombay or Areca Catechu; and Mangrove Cutch."

"Catechin; $C_{15}H_{14}O_6 \cdot 4H_2O$; the crystalline principle, was first described by Nees Van Esenbeck (Annalen; 1832; I, 243), was sub-

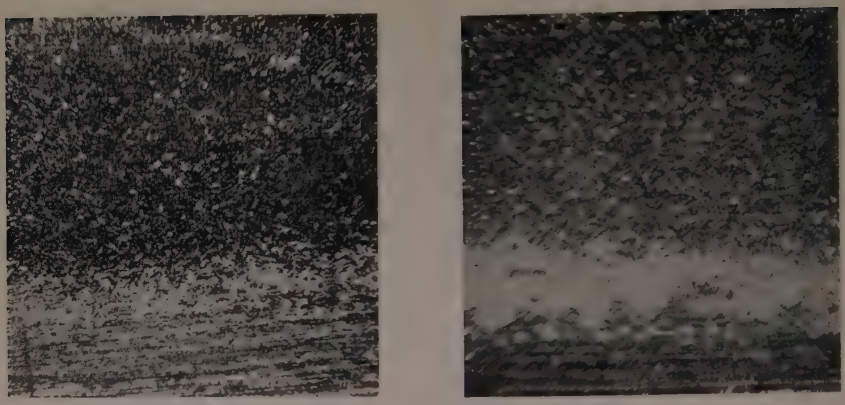
sequently examined by Berzelius in 1837 (Jahres; 14, 235), and more recently by numerous chemists."

"Mangrove Tannin;$C_{24}H_{26}O_{12}$. This important tannin is derived from the Rhizophora Mangle (Linn.), R. Mucronata (Lam.); Ceriops Candolleana (Arn.); C. roxburghinna (Arn.) and other allied species. It is described as an amorphous red powder, which, on fusion with alkali, gives protocatechuic acid, and with boiling dilute sulphuric acid, the phlobophene $C_{48}H_{46}O_{21}$ . . . . . This tannin closely resembles in its properties catechutannic acid (see Catechu), and indeed Mangrove Cutch and Catechu may be employed in many cases for the same purpose. Possibly these two substances are identical, and Procter (private communication) has isolated from Mangrove Cutch a small quantity of a colorless crystalline substance resembling Catechin."

Consequently, pure catechin was obtained and tested as an inhibitor. It was isolated from japonic in the following manner: Finely powdered japonic was extracted with ten times its weight of boiling ethyl acetate, the solution evaporated, and the residue crystallized from ten times its weight of water. The product was again dissolved in boiling water, and a lead acetate solution added, drop by drop, until a colored precipitate was no longer formed, and the filtrate was almost colorless. The latter, while hot, was treated with H_2S, the PbS removed, and the crystals, which separate on cooling, were collected, washed, and allowed to dry at room temperature.

Catechin formula	Lit. M.P.	Expt. M.P.
	205 deg. F.	205 deg. F.

The catechin obtained was very pure. It was colorless, and possessed a sharply defined melting point at 205 deg. F. This melting point was for the catechin having the formula just given with 4 molecules of water of crystallization. This, when tested in the boiler, gave the results indicated by the photomicrograph in Fig. 16. It is quite apparent that catechin, which is similar in character to the tannins in many respects and often occurs with them, does not have scale-inhibiting effect. The tannin remaining after the extraction of the catechin retained its inhibiting power.



Catechin Blank

FIG. 16. PHOTOMICROGRAPHS OF SCALE FORMED WITH AND WITHOUT CATECHIN PRESENT
20 x

Isolation of the Pure Tannin

The following method is one commonly used in isolating pure tannin: "All the well known tannins are dissolved by hot water, and yield precipitates with lead acetate solution, and thus by decomposing the well-washed lead precipitate from a plant infusion in the moist condition with H_2S, a crude solution of the tannin is obtained. This can be concentrated in vacuo over caustic potash or sulphuric acid. . . . . As, however, the tannin usually exists in the plant side by side with yellow colouring matter, either in the free state or as glucoside, and other secondary substances soluble in water, a fractional precipitation with lead acetate is preferably adopted, in which the middle portion usually yields the purest tannin."

A combination of this method and the one used by Dr. Russell was adopted, as is outlined in Chart IX.

Figure 17 shows the results obtained and indicates that purified tannin exhibited no noticeable improvement over the crude extract. The method of isolation described did not prove feasible for the more soluble extracts. The tannins from these extracts were, however, purified by the method used by Dr. Russell, but were never tested in the boilers, since the test described indicated that this purification would not result in any decided improvement over the original extract.

The information available in the literature concerning reactions of tannins strengthens the assumption that a break down of the tannin molecule occurs in the boiler. Several tests are available for the

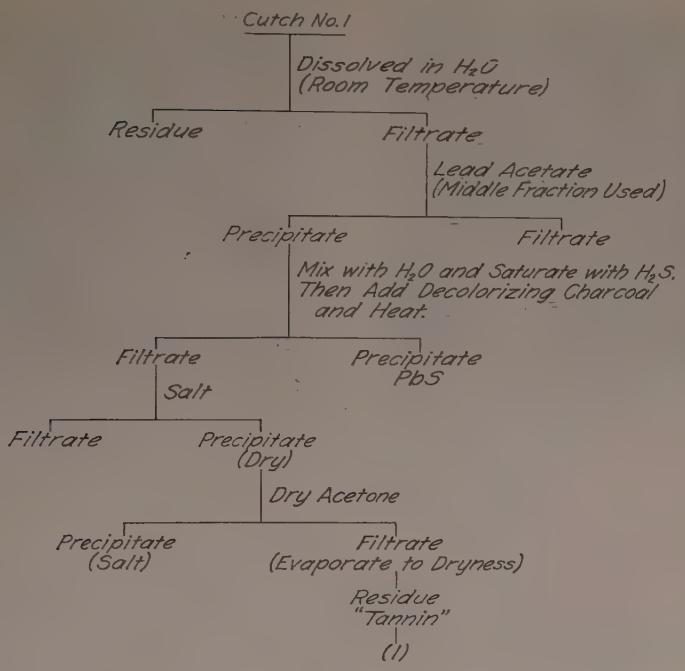


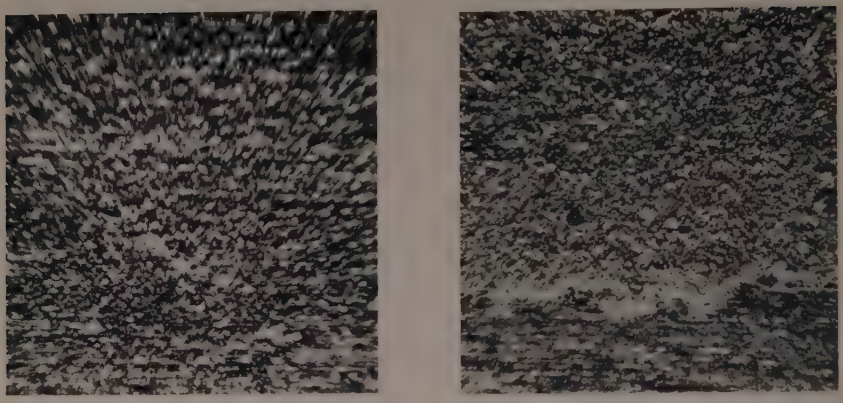
CHART IX

determination of tannin stability under conditions of extreme heat, but are not exactly analogous to the conditions under consideration. The fusion tests which lead to a complete break down are too extreme. One test often used and which seems to involve only the temperature effect upon tannins is the glycerol test, which is as follows:

Heating with Glycerol

One gram of the tannin is heated with 5 cc. of glycerol, the temperature being slowly raised from 320 deg. F., and kept for one-half hour between 392-410 deg. F. The product, diluted with 20 cc. of water, is extracted with ether, the extract evaporated, and the residue tested for pyrogallol or catechol.

Since glycerol $\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}$ is a viscous inert substance boiling at 554 deg. F., no reaction between it and the tannin will occur, but rather it serves as a solvent which will permit extreme heat to be applied to the tannin. Therefore, the glycerol test was used to gain some



Purified Tannin Blank

FIG. 17. PHOTOMICROGRAPHS OF SCALE FORMED WITH AND WITHOUT PURIFIED TANNIN PRESENT
20 x

idea of what change the phlobatannin molecule might undergo at higher temperatures. When the temperature of the glycerol and tannin mixture reached 320 deg. F., a strong evolution of gas started which continued during the three hours of heating. The two tannins used were chestnut extract and cutch No. 1. Since it was known that the broken-down tannin material that finally results in the flask is composed of pyrogallol, catechol, and similar simple hydroxy benzene derivatives, attempts were made to obtain information as to the nature of the gas evolved. Decomposition material other than pyrogallol and catechol and other phenolic compounds undoubtedly remained in the flask. Since the phenolic compounds do not display the strong inhibiting properties of the extracts at higher alkalinity, but do display, on the other hand, as strong or stronger inhibiting ability at lower alkalinity, it seemed probable that, if a break-down of the molecule took place in the boiler, it was not completely to the phenolic compounds of the pyrogallol type. Since the ultimate or complete break-down does lead to phenolic compounds, the assumption that the breakdown is of an intermediate nature is necessary to explain the discrepancy between the effect of the tannin extract and the hydroxy benzene derivatives as inhibitors at the higher alkalinity.

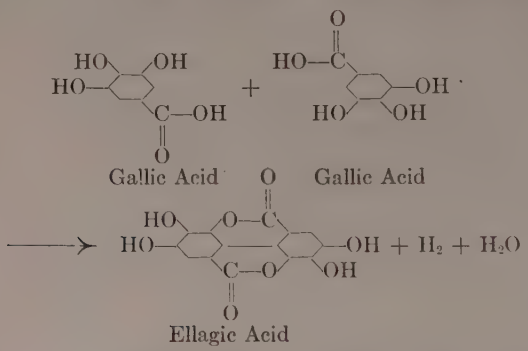
The fact that an evolution of gases occurred indicated that decomposition started at this temperature, 320 deg. F. The phlobatannin structure previously given* would suggest that the gas evolved

*See page 59.

might be some one of the following: hydrogen, carbon monoxide, carbon dioxide, unsaturated hydrocarbons, or formaldehyde. By passing the evolved gas through suitable reagents, most of these possibilities were eliminated. The first reagent through which the gas was bubbled was a $BaCl_2$-$KMnO_4$ solution. If carbon dioxide was being evolved, a precipitate of barium carbonate should have formed, but none was observed; this eliminated the possibility of the evolved gas being carbon dioxide. Had the gas been carbon monoxide, the $KMnO_4$ solution would have oxidized the carbon monoxide to carbon dioxide, and a barium carbonate precipitate would have been obtained. No precipitate was obtained; however, the $KMnO_4$ solution was decolorized, indicating the presence of an oxidizable gas other than carbon monoxide. Furthermore, the decolorization was not due to hydrogen, since $KMnO_4$ solution is only decolorized by nascent hydrogen. However, a considerable amount of the gas was not dissolved by the reagent, and this gas passing unaffected through the reagent must have been hydrogen. The gas causing the decolorization of the $KMnO_4$ could have been, it seems, an unsaturated hydrocarbon or formaldehyde. The decomposition involved probably the elimination of hydrogen, formaldehyde, or an unsaturated hydrocarbon. The identification of the gas could have been made with additional work.

As was previously stated, extreme conditions would carry the decomposition to phenolic compounds, but undoubtedly the decomposition never reaches that stage but probably stops at a relatively stable intermediate compound for the reason previously cited. This evidence is given in support of the idea that the tannin, as such, does not exist at the end of a test, and that the effective inhibitor is a compound resulting from the decomposition of tannin. This would explain the discrepancy between the various phlobatannins. While the various phlobatannin molecules bear a close relationship to each other, their decomposition products might vary widely. The phlobatannin molecule has been synthesized by Russell, as previously stated. There is little room for doubting the structure that he has given, since he started with simple known organic compounds and built up the molecule stepwise. A piece of cleaned and scraped sheepskin immersed in a concentrated solution of this synthesized tannin showed no sign of decomposition after four months, and assumed the characteristics of leather. Since the compound also gave the same type reactions as a naturally-occurring phlobatannin such as hemlock, there is little doubt that the structure assigned it represents the general structure of a phlobatannin.

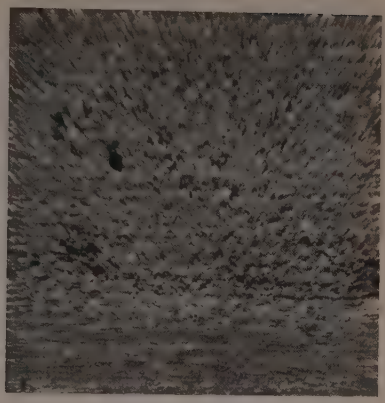
Therefore, since both hemlock and chestnut are phlobatannins, they would be expected to have approximately the same inhibiting power, provided they remained as such throughout a test run. Likewise, if the break-down of the tannin is completely to phenolic compounds, then their inhibiting power should still be about the same, since none of the phenolic compounds are effective at the higher alkalinity. Traces of ellagic acid have been reported found in chestnut extracts, and, since this was thought to be a possible explanation for the different results obtained, myrobalan extract containing from 30 to 40 per cent of ellagic acid was tested and the results were negative. The formation of ellagic acid is represented thus:



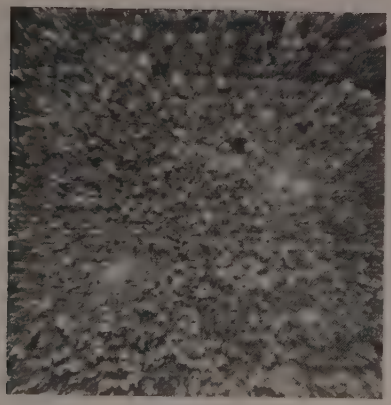
In view of this possible reaction, a gallic acid and potassium permanganate combination was tried in the boiler, and a remarkably clean tube obtained, as is evident from an examination of Fig. 18.

The results shown were not due to the ellagic acid formed, as shown in the equation, but to the additive effect of the gallic acid-potassium permanganate mixture. Since no gallic acid is obtainable from a phlobatannin, the indicated reaction would not occur and no ellagic acid would be expected. While the ellagic acid hypothesis might possibly explain the discrepancy between chestnut and hemlock, it does not help to account for the effectiveness of cutch No. 1. This cutch, while a phlobatannin, or at least giving all the characteristic reactions of a phlobatannin, differs widely from the other extracts used. It is with difficulty soluble in water, while it dissolves readily in a slightly alkaline solution. Its inhibiting power is not as sensitive to a change of alkalinity as that of the other extracts. Cutch No. 1 is remarkably stable toward alkali. After boiling with 1 normal NaOH for several hours, its inhibiting power was not affected to any great extent. Its inhibiting effect, however, was easily destroyed by boiling

Blank



Gallic Acid—$KMnO_4$



$KMnO_4$ Blank
Alkalinity 3 mm. per liter in each case

FIG. 18. PHOTOMICROGRAPHS OF SCALE FORMED AFTER OXIDIZING ORGANIC MATERIAL
20 x

with dilute HCl, as will be noticed by referring to the miscellaneous chart. This undoubtedly is due to phlobophene formation, which further demonstrates its phlobatannin character. This phlobophene has no iron-greening or iron-blueing property.

Table 81 lists the tannin classification reactions. The three large classes of tannin are: phlobatannins, gallotannin, and ellagitannin. The class gallotannin has a sole member, which is what is commonly called tannic acid. Ellagitannin was not available. Myrobalan extract, previously mentioned, is an example of that type of tannin. All

TABLE 81
COMPARISON OF TANNIN REACTIONS

Reagent Added	Cutch			Hemlock Extract	Chestnut Extract	Japonic	Gallo-tannin
	No. 1	No. 2	No. 3				
Alcoholic ferric chloride	Green solution	Green solution	Green solution	Green solution	Blue solution	Green solution	Dark-blue-black ppt.
Aqueous ferric chloride	Green solution	Green solution	Blue solution	Dark ppt.	Blue solution	Green solution	Dark-blue-black ppt.
Gelatin	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.
Lead acetate	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.	Ppt.
Boiling 5 per cent hydrochloric acid	Brown ppt.	Red ppt.	.....	Brown ppt.	.....	.....	No ppt.
Bromine water	Yellow ppt.	Ppt.	No ppt.	Ppt.	No ppt.	Yellow ppt.	No ppt.
Slaked lime	Pink solution	Pink solution	Slight ppt. tinged with pink	Faint pink solution	No visible effect	Pink solution	Ppt.
Sodium sulphite	Very faint pink solution	Pink solution	Pink solution	Pink solution	Bright pink solution	Murky	No visible effect
Copper sulphate	Murky green solution	Murky	Murky	Green solution	No visible effect	Light green solution	Light green ppt.
Aqueous ammonia	Darkening	Darkening	Darkening	Darkening	Darkening	Darkening	Darkening
Formaldehyde + hydrochloric acid	Ppt. on warming	Ppt. on warming	No ppt.	Ppt. on warming	No ppt. on warming	Ppt. on warming	No ppt.
Potassium dichromate solution	Dark brown ppt.	Dark brown ppt.	Brown ppt.	Brown ppt.	Brown ppt.	Brown ppt.	Brown ppt.

Calcium Sulphate Scale Studies in Scaling Boiler

Alkalinity given in millimoles per liter of NaOH. Amount of inhibitor, 100 p.p.m. All tests made in experimental unit.

Pyrogallol Type Materials				Tannin Materials			Miscellaneous Materials		
Inhibitor		Alkalinity	Preventive Effect	Inhibitor	Alkalinity	Preventive Effect	Inhibitor	Alkalinity	Preventive Effect
	Catechol	0.5 3	Fair Unsatisfactory	Catechin	3	Unsatisfactory	Quercitin	3	Unsatisfactory
	Hydro-quinone	0.5 3	Unsatisfactory Unsatisfactory	Tannic Acid or Gallotannin	3	Unsatisfactory	Tetra-hydroxy Chalkone	3	Unsatisfactory
	Quinone	3	Unsatisfactory	No. 1 Cutch	0.5 3 6	Good Fair Fair	Na_2SO_3 100 p.p.m. Pyrogallol	3	Unsatisfactory
	Pyrogallol	0.5 3 6	Good Fair Unsatisfactory	No. 2 Cutch	3	Unsatisfactory	200 p.p.m. Pyrogallol	3	Fair
	Phloro-glucinol	3	Unsatisfactory	No. 3 Cutch	3	Unsatisfactory	Phyenylene Di-Amine Alkalinity Pyrogallol	6	Fair
	Picric Acid	3	Unsatisfactory	Japonic	3	Unsatisfactory			
	Tri-nitro Toluene	3	Unsatisfactory	Chestnut extract	3	Fair			
				Hemlock extract	3	Unsatisfactory			
				Chesco-extract	3	Unsatisfactory			
				Mimosa Tannin	3	Unsatisfactory			
				No. 1 Cutch Tannin	3	Fair			

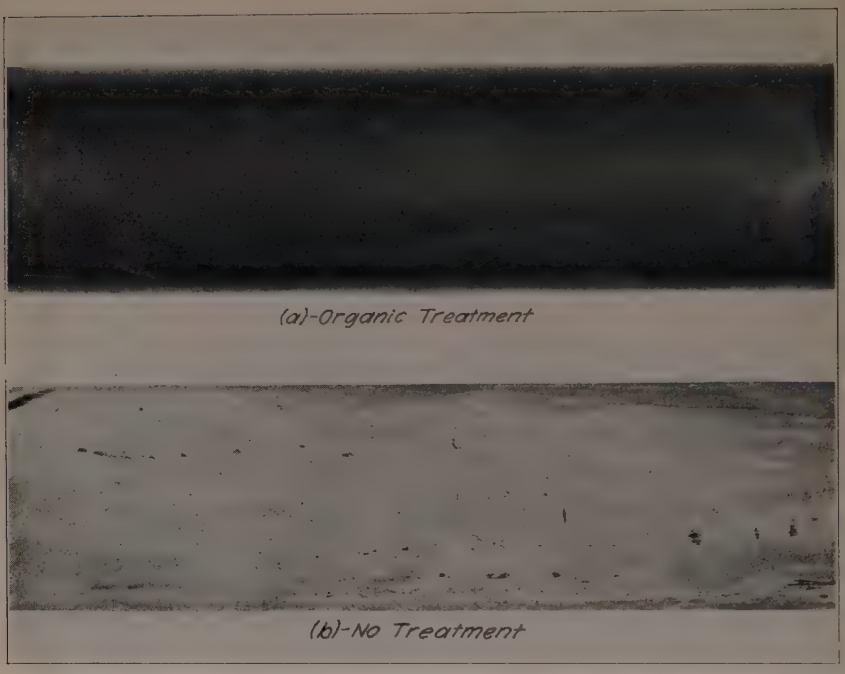


FIG. 19. EFFECT OF ORGANIC TREATMENT ON CALCIUM SULPHATE SCALE

remaining tannins encountered have been phlobatannins of various types. In the table, only two classes are represented, namely, gallotannin and phlobatannin. This table is inserted to bear out the distinction that is made between gallotannin and phlobatannin.

Table 82 gives a summary of the results of the tests made on various materials tested in the scaling boiler. Figure 19 shows photographic views of tubes, and illustrates the action of organic material in stopping the formation of calcium sulphate scale.

Conclusions

A summary of conclusions is as follows:

(1) The inhibiting power of the pure tannin and the crude extract is practically the same.

(2) A reduction of alkalinity in the case of sulphate scale greatly increases the inhibiting property of the tannins, pyrogallol, etc.

(3) The inhibiting power of tannins, pyrogallol, and phenolic compounds is not noticeably affected by any change of alkalinity in the case of calcium silicate scale.

TABLE 83
EFFECT OF SODIUM HYDROXIDE ON CALCIUM SILICATE SCALE FORMATION
Time of test, 46 hours
Pressure, 225-250 lb. per sq. in.

SiO_2 millimoles per liter	$CaSO_4$ millimoles per liter	$\frac{SiO_2}{CaSO_4}$	NaOH millimoles per liter	Scale
5.0	5.0	1	6	Very heavy
2.5	2.5	1	6	Heavy
2.5	2.5	1	3	Heavy
1.6	0.8	2	6	Heavy
1.6	0.8	2	3	Heavy
1.6	1.6	1	6	Heavy
1.6	1.6	1	3	Heavy
1.6	1.6	1	1.5	Heavy

(4) The inhibiting power of the tannins, pyrogallol, etc., is not due primarily to holding the calcium in solution. The concentration of calcium sulphate in the boiler water at the start of a test was 500 parts per million. At the end of a test, the calcium sulphate concentration in solution varied approximately from 8 parts per million to 80 parts per million. In any case, however, at least 420 parts per million of calcium sulphate must have left the solution, coming out in the form of a scale or sludge.

(5) The catechin occurring in many of these extracts is not responsible for the scale-inhibiting property displayed by the extract.

(2) Silicate Scale Tests

Tests were run in the laboratory boiler at 250 lb. per sq. in. in which calcium silicate scale was formed by adding calcium sulphate and sodium metasilicate to the boiler water.

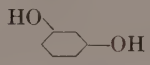
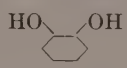
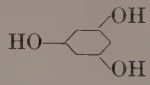
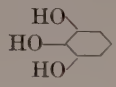
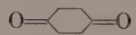
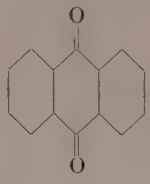
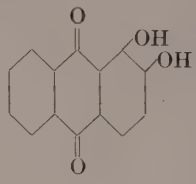
By treating the feed water with pyrogallol or cutch so that the resulting concentration was 100 p.p.m., the formation of scale could be stopped at alkalinities varying from 1 to 6 millimoles per liter. As in the case of calcium sulphate scale, it was necessary to determine the effect of increased alkalinity on the formation of calcium silicate. The alkalinity is not the controlling factor in this particular scale deposition, but rather the concentration and molal ratio of calcium to silica. Table 83 and Fig. 20 show the results obtained. Since pyrogallol showed definite inhibiting power, a series of tests on phenolic compounds gave the results shown in Table 84.

Figure 21 illustrates the inhibiting power of the phenolic compounds, showing the increase in inhibiting power with increase in OH groups in the ring.

TABLE 84

EFFECT OF PHENOLIC COMPOUNDS IN PREVENTING CALCIUM SILICATE SCALE FORMATION

Time of Test, 46 hours
Pressure, 225-250 lb. per sq. in.
Amount of inhibitor, 100 p.p.m.

Inhibitor Used	Formula	Preventive Effect
Phenol		No effect
Resorcinol		Fair
Hydroquinone		Fair
Catechol		Fair
Phloroglucinol		Good
Pyrogallol		Very good
Quinone		Good
Anthraquinone		No effect
Alizarine		No effect

The larger molecules such as anthraquinone and alizarin have no effect whatsoever.

Table 85 shows the effect of various tannin materials in inhibiting calcium silicate scale formation. The fact that cutch No. 1 showed the same inhibiting power at 100 and 50 p.p.m. indicates that there

TABLE 85

EFFECT OF TANNIN MATERIALS IN PREVENTING CALCIUM SILICATE SCALE FORMATION

Time of test, 46 hours
Pressure, 225-250 lb. per sq. in.
Amount of inhibitor, 100 p.p.m.

Inhibitor Used	Preventive Effect	Inhibitor Used	Preventive Effect
Gallotannin	Good	Hemlock extract	Fair
Cutch No. 2	Good	Cutch No. 1—100 p.p.m.	Good
Chestnut extract	Good	Cutch No. 1—50 p.p.m.	Good

is probably not a stoichiometric relation necessary, but that the action is mechanical.

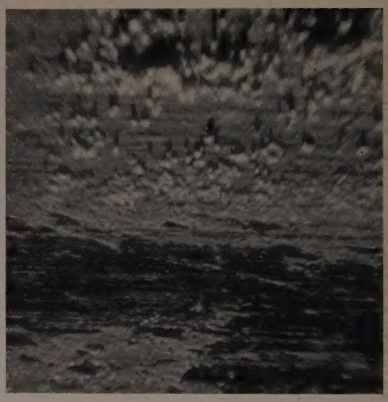
Only a few tests were run on sodium-alumino silicate scale. It has been shown that the ratio of silica to alumina is 4 in analcite. Although this ratio is present in analcite, the existing concentration in the feed water does not have to be at this ratio for a sodium-alumino silicate to form. Analysis of a sodium-alumino silicate scale showed the following: 54.3 per cent SiO_2, 27.4 per cent Al_2O_3, and 7.53 per cent H_2O, or a ratio of silica to alumina of 3.36 and of silica to water of 2.16, which agrees well with that ratio of constituents in analcite. Analysis of the blow down showed the ratio of silica to alumina lost from solution to be 5.5.

Sodium-alumino silicate scales are very firm, tenacious, and heat-resisting, and cannot be removed from the heating tube easily. The controlling factor in the formation of heavy sodium-alumino silicate scale is the temperature. Attempts at forming the scale at temperatures corresponding to 250 lb. per sq. in. gage were futile, while temperatures corresponding to 750 lb. per sq. in. to 900 lb. per sq. in. gave a very definite scale. Cutch No. 2 seemed to affect the formation of the sodium-alumino silicate scale to the greatest degree. Pyrogallol and cutch No. 1 had very little effect, while cutch No. 2 seemed to cause the formation of a soft scale, which could be removed easily.

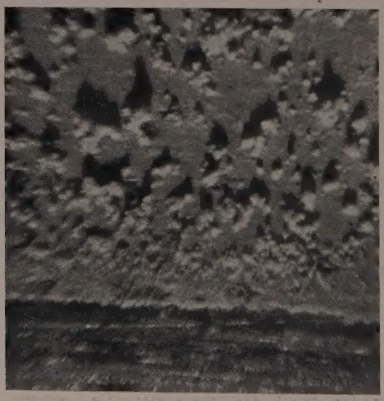
Figure 22 shows clearly the effect of the organic material on the scale formed.

10. *Conclusions Drawn from Organic Studies.*—Particular conclusions have already been stated in the various sections of this report, consequently, only the main conclusions will be summarized here.

$CaSO_4$—1.67 millimoles per liter
SiO_2 —1.67 millimoles per liter
NaOH—6. millimoles per liter



$CaSO_4$—1.67 millimoles per liter
SiO_2 —1.67 millimoles per liter
NaOH—3. millimoles per liter

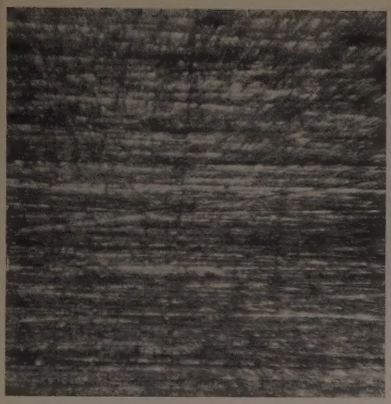


$CaSO_4$—1.67 millimoles per liter
SiO_2 —1.67 millimoles per liter
NaOH—1.5 millimoles per liter

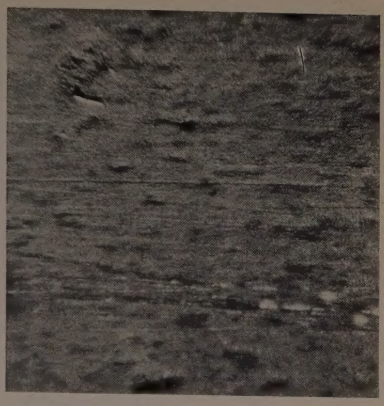
FIG. 20. PHOTOMICROGRAPHS OF SILICATE SCALE
20 x

In the treatment of water causing calcium sulphate or carbonate scale at 212 deg. F., various organic materials appear to be effective. Pure organic materials have been found effective in preventing this type of scale, and a study has been made of the structural arrangement of the most effective organic material.

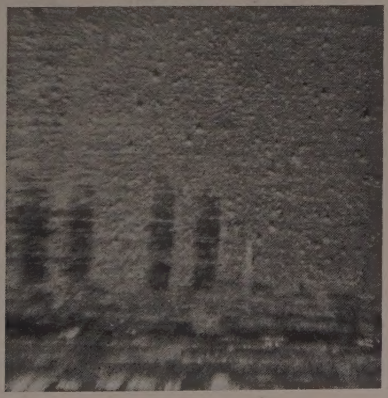
The organic material which was effective in preventing scale at 212 deg. F. was found to increase the solubility of calcium carbonate.



$CaSO_4$—1.67 millimoles per liter
SiO_2 —1.67 millimoles per liter
NaOH—6. millimoles per liter
Pyrogallol—100 parts per million



$CaSO_4$—1.67 millimoles per liter
SiO_2 —1.67 millimoles per liter
NaOH—6. millimoles per liter
Catechol—100 parts per million



$CaSO_4$—1.67 millimoles per liter
SiO_2 —1.67 millimoles per liter
NaOH—6. millimoles per liter
Phenol—100 parts per million

FIG. 21. PHOTOMICROGRAPHS OF CALCIUM SILICATE SCALE
20 x

The tests run in the scaling boiler at steam pressures between 250 and 900 lb. per sq. in. showed that pyrogallol, gallic acid, and similar types of organic material were very effective in preventing calcium sulphate scale. If the alkalinity was kept low, the organic material was more active. Calcium silicate scale was also prevented by means of the organic treatment. However, the alkalinity of the boiler did

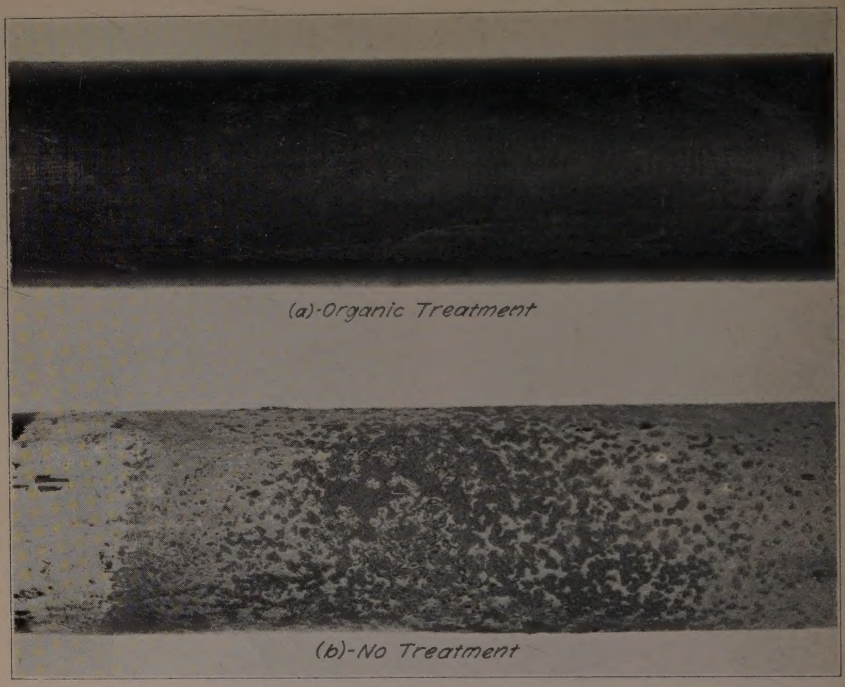


FIG. 22. EFFECT OF ORGANIC TREATMENT ON SILICATE SCALE

not influence this action. Sodium aluminum silicate scale was produced at the higher steam pressures and was also prevented by the action of the organic material.

These results on scale prevention indicate that the use of organic treatment might prove very effective if properly controlled. This initial research has merely given a broad outlook on the great possibilities of this field of water treatment. With this as a foundation, there is a possibility that further properly directed research along this line would give favorable results.